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FABRICATION AND TESTING FOR SOLAR DETOXIFICATION PROJECT

FINAL REPORT

Task Order 3
December 1997

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Prepared by:

SCIENCE APPLICATIONS INTERNATIONAL CORPORATION
ENERGY PROJECTS DIVISION
15000 W. 6th Ave., #202
Golden, Colorado 80401

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Final Report

Task Order 3 Fabrication and Testing For Solar Detoxification Project

Contributors to this Report: S. Doty, N. Widmer, K. Beninga, J. Cole

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Prepared by: Science Applications International Corporation
Energy Products Division
15000 W. 6th Avenue, Suite 202
Golden, Colorado 80401

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13. ABSTRACT

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The demonstration test used a surrogate waste mix of seven VOCs and one SVOC representative of common soil contaminants at U.S. Army remediation sites. A total of nine tests were conducted during the demonstration to evaluate system performance. Six tests were conducted to define the system's operating envelope, and three replicated tests were conducted at center point conditions to establish the process repeatability and improve statistical analysis. Stoichiometry, or air to waste ratio, was varied from 1.2 to 1.4, as required for stoichiometric combustion, while surrogate waste feed rates were held constant. Solar insolation was varied from the design's maximum solar input of approximately 200,000 British thermal units per hour (BTU/hr) to 0 BTU/hr.

The presence of VOCs and SVOCs, including polychlorinated dibenzodioxins/polychlorinated dibenzofurans (also known as dioxins/furans, or PCDD/PCDF), emitted from the solar reactor were used to determine the system's destruction efficiency (DE) and the ability to comply with regulatory standards for thermal treatment units. Analytical samples of the solar reactor flue gases were also used to determine production rates for products of incomplete combustion (PICs), including 33 VOCs, 33 SVOCs, PCDD/PCDF, total hydrocarbons (THC), oxides of nitrogen (NO_x), carbon monoxide (CO), and hydrochloric acid (HCl). PIC concentrations were required to be at or below levels observed for comparable hazardous waste incineration units and meet appropriate standards.

The solar detoxification system was designed to operate with residence times and reactor temperatures of approximately 1 second and 700°C (1292°F) to 1000°C (1832°F), respectively. Initial testing identified problems with flame stability in the reactor under those design conditions. Operating conditions were adjusted, resulting in longer residence times on the order of 4 seconds and lower reactor temperatures of approximately 480°C (900°F) to 650°C (1200°F). Even at the lower operating temperatures, the solar detoxification system was able to achieve an average DE of over 99.99 percent for the 8 surrogate compounds, and meet the demonstration objective DE of 99.99 percent for total POHCs in 8 of 9 tests. The DE for one surrogate VOC, carbon tetrachloride, ranged from 99.95334 to 99.99653 percent under the test conditions. Within the test limitations, a statistically significant impact could not be directly attributed to the input of solar energy to the system: average DEs obtained during on-sun testing, using stoichiometries of 1.2 to 1.4, ranged from 99.99685 to 99.99951 percent; average DEs for off-sun testing, using the same stoichiometries, ranged from 99.99962 to 99.99981 percent. Interpretation of these subtle differences was further complicated because DEs greater than 99.99 percent may be attributable to high analytical detection limits observed during the test. Based on the current data, the DEs for the 8 POHCs were not improved by solar input.

It was anticipated that solar detoxification would generate significantly lower levels of PICs than measured in emissions from commercial incinerators. The system did not achieve this during the Demonstration Test. Test data could not be used to positively identify the cause(s) of the higher than anticipated PIC formation. It is possible these measurements were affected by specific design features of the test assembly [e.g., higher than normal exhaust duct gas temperature and the length (80 to 100 feet) of the exhaust duct]. Additional design and testing would be required to confirm this. The emissions from the reactor were above standards for the specific PICs PCDD/PCDF, however actual emissions to the atmosphere are expected to be lower in an optimized operating system, since additional treatment steps would occur. In general, these tests indicate the system produced PICs at levels comparable to commercial incineration units, consistent with the test objective.

The system met test objectives for other pollutant emissions. As expected, the reactor produced very low NO_x emissions, meeting the NSPS and medical waste standards during all 9 tests; this was likely due to the low operating temperature range. Emissions of THC and HCl were also below regulatory standards, meeting the objectives for the demonstration. CO emissions varied from 12 to 673 parts per million by volume (ppmv) during the tests, but met the regulatory goal of 50 ppmv during 5 of the 9 tests. There was some indication that low stoichiometry and high solar insolation may reduce CO emissions; however, optimization studies are needed to determine if CO may be properly controlled during operations.

This test series demonstrated a number of key aspects of the solar detoxification technology. For example, the tests successfully demonstrated such key factors as efficient solar collection, concentration, and integration of solar energy input into a waste detoxification system. Other aspects of system design and analytical protocols will require improvement before final conclusions are reached about the ultimate effectiveness of this type of system for destruction of organics removed from contaminated soils. System response to varying types of waste inputs and the system controls necessary to ensure performance under varying solar input conditions are two important areas requiring further investigation. Analysis of the test results identified several design changes that are expected to improve system control and performance. These include changes to the reactor wall design to improve flame stability and combustion performance, elimination of the duct that potentially interfered with PIC measurements, and improvement in flame detection. Analytical detection limits also require further improvement to support the quantitative precision and accuracy necessary to evaluate differences in DEs observed between on-sun and off-sun operations with high statistical confidence. Implementation of these changes may permit system operation and evaluation under more optimal conditions that support quantitative evaluation of the true impact of solar insolation on destruction efficiencies for VOCs and SVOCs.

EXECUTIVE SUMMARY

A demonstration of a solar detoxification system was conducted for the U.S. Army Environmental Center (USAEC) at Science Applications International Corporation's (SAIC's) test site near Golden, Colorado, in June 1997. The purpose of this demonstration test was to evaluate the use of solar energy for thermally detoxifying organic compounds representative of soil contamination found at U.S. Army sites. The demonstration test was carried out under the third of three tasks conducted under contract by SAIC. Under Tasks 1 and 2, the conceptual and detailed design of a pilot-scale system was completed. Under Task 3, fabrication and testing of the system were accomplished. This document presents the results obtained during the Task 3 demonstration test.

The purpose of this demonstration test was to evaluate the use of solar energy to thermally detoxify organic compounds removed from contaminated media by *ex situ* (such as thermal desorption) or *in situ* (such as soil vapor extraction) treatment systems, or desorbed from pretreatment matrices (such as activated carbon). Extraction systems are commercially available so the step of directly extracting organics from contaminated soil was excluded from the pilot-scale demonstration. Rather, the pilot-scale demonstration test focused on evaluating ultraviolet (UV)-rich solar destruction of volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) by a solar incinerator and the environmental control of the resulting off-gases.

The demonstration test used a surrogate waste mix of seven VOCs and one SVOC representative of common soil contaminants at U.S. Army remediation sites. A total of nine tests were conducted during the demonstration to evaluate system performance. Six tests were conducted to define the system's operating envelope, and three replicated tests were conducted at center point conditions to establish the process repeatability and improve statistical analysis. Stoichiometry, or air to waste ratio, was varied from 1.2 to 1.4, as required for stoichiometric combustion, while surrogate waste feed rates were held constant. Solar insolation was varied from the design's maximum solar input of approximately 200,000 British thermal units per hour (Btu/hr) to 0 Btu/hr.

The presence of VOCs and SVOCs, including polychlorinated dibenzodioxins/polychlorinated dibenzofurans (also known as dioxins/furans, or PCDDs/PCDFs), emitted from the solar reactor were used to determine the system's destruction efficiency (DE) and the ability to comply with regulatory standards for thermal treatment units. Analytical samples of the solar reactor flue gases were also used to determine production rates for products of incomplete combustion (PICs), including 33 VOCs, 33 SVOCs, PCDDs/PCDFs, total hydrocarbons (THC), oxides of nitrogen (NO_x), carbon monoxide (CO), and hydrochloric acid (HCl). PIC concentrations were required to be at or below levels observed for comparable hazardous waste incineration units and to meet appropriate standards.

The solar detoxification system was designed to operate with residence times and reactor temperatures of approximately 1 second and 700°C (1,292°F) to 1,000°C (1,832°F), respectively. Initial testing identified problems with flame stability in the reactor under those design conditions. The initial results showed that the system would not operate without a liquefied petroleum gas (LPG) pilot flame continuously supplying approximately 30,000 Btu/hr to the

solar reactor. Operating conditions were adjusted, resulting in longer residence times on the order of 4 seconds and lower reactor temperatures of approximately 480°C (900°F) to 650°C (1,200°F). Even at the lower operating temperatures, the solar detoxification system was able to achieve an average DE of over 99.99 percent for the eight surrogate compounds, and meet the demonstration objective DE of 99.99 percent for total principle organic hazardous constituents (POHCs) in eight of nine tests. The DE for one surrogate VOC, carbon tetrachloride, ranged from 99.95334 to 99.99653 percent under the test conditions. Within the test limitations, a statistically significant impact could not be directly attributed to the input of solar energy to the system: average DEs obtained during on-sun testing, using stoichiometries of 1.2 to 1.4, ranged from 99.99685 to 99.99951 percent; average DEs for off-sun testing, using the same stoichiometries, ranged from 99.99962 to 99.99981 percent. Interpretation of these subtle differences was further complicated because DEs greater than 99.99 percent may be attributable to high analytical detection limits observed during the test. Based on the current data, the DEs for the eight POHCs were not improved by solar input.

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The system met test objectives for other pollutant emissions. As expected, the reactor produced very low NO_x emissions, meeting the New Source Performance Standard (NSPS) and medical waste standards during all nine tests; this was likely due to the low operating temperature range. Emissions of THC and HCl were also below regulatory standards, meeting the objectives for the demonstration. CO emissions varied from 12 to 673 parts per million by volume (ppmv) during the tests, but met the regulatory goal of 50 ppmv during five of the nine tests. There was some indication that low stoichiometry and high solar insolation may reduce CO emissions; however, optimization studies are needed to determine if CO may be properly controlled during operations.

This test series demonstrated a number of key aspects of the solar detoxification technology. For example, the tests successfully demonstrated such key factors as efficient solar collection, concentration, and integration of solar energy input into a waste detoxification system. Other aspects of system design and analytical protocols will require improvement before final conclusions are reached about the ultimate effectiveness of this type of system for destruction of organics removed from contaminated soils. System response to varying types of waste inputs and the system controls necessary to ensure performance under varying solar input conditions are two important areas requiring further investigation. Analysis of the test results identified several design changes that are expected to improve system control and performance. These changes include: modifying the reactor wall design to improve flame stability and combustion performance and eliminate the LPG pilot flame, eliminating the duct that potentially interfered

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LIST OF ACRONYMS AND ABBREVIATIONS

2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo(p)dioxin
ASTM	American Society for Testing and Materials
BFI	Browning Ferris Industries
Btu	British thermal units
Btu/hr	British thermal units per hour
CAA	Clean Air Act
CDPHE	Colorado Department of Public Health and Environment
CEMS	Continuous Emission Monitoring System
Cl₂	chlorine
CO	carbon monoxide
CO₂	carbon dioxide
CPVC	chlorinated polyvinyl chloride
1,2-DCB	1,2-dichlorobenzene
DCF	discounted cash flow
DE	destruction efficiency
DQO	data quality objective
DRE	destruction and removal efficiency
dscf	dry standard cubic feet
dscm	dry standard cubic meter
EER	Energy and Environmental Research Corporation
FD	forced draft
FID	flame ionization detector
FRP	fiber reinforced polyester
GC/MS	gas chromatography/mass spectrometry
GFIR	gas filter infrared
gph	gallons per hour
gpm	gallons per minute
gr	gram
HCl	hydrochloric acid
hp	horsepower
HRGC/HRMS	high resolution capillary column gas chromatography/high resolution mass spectrometry

LIST OF ACRONYMS AND ABBREVIATIONS (Continued)

HRGC/LRMS	high resolution gas chromatography/low resolution mass spectrometry
HRMS	high resolution mass spectrometry
ID	induced draft
IR	infrared
IRDMIS	Installation Restoration Data Management Information System
kBtu/hr	thousand British thermal units per hour
kW	kilowatt
LPG	liquefied petroleum gas
LRMS	low resolution mass spectrometry
MACRS	Modified Accelerated Cost Recovery System
mmBtu/hr	million British thermal units per hour
NaCl	sodium chloride
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
NDIR	nondispersive infrared
ng	nanograms
ng/dscm	nanogram per dry standard cubic meter
NIP	normal incidence pyrheliometer
NIST	National Institute of Standards and Technology
nm	nanometers
NO_x	oxides of nitrogen
NSPS	New Source Performance Standard
O₂	oxygen
OD	outside diameter
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzodioxin, also referred to as dioxin
PCDF	polychlorinated dibenzofuran, also referred to as furan
PCP	pentachlorophenol
PIC	products of incomplete combustion
PLC	programmable logic controller
POHC	principal organic hazardous constituent
ppm	parts per million
ppmv	parts per million by volume
psig	pounds per square inch gauge

LIST OF ACRONYMS AND ABBREVIATIONS (Continued)

QA	quality assurance
QA/QC	quality assurance/quality control
QAPjP	Quality Assurance Project Plan
QC	quality control
RCRA	Resource Conservation and Recovery Act
ROI	return on investment
RPD	relative percent difference
RSD	relative standard deviation
SAIC	Science Applications International Corporation
scf	standard cubic feet
scfh	standard cubic feet per hour
scfm	standard cubic feet per minute
SMVOC	sampling method for volatile organic compounds
SO ₂	sulfur dioxide
SOE	secondary optical element
SS	stainless steel
SVE	soil vapor extraction
SVOC	semivolatile organic compound
SWSS	surrogate waste storage system
TCE	trichloroethylene
TEQ	toxic equivalent
THC	total hydrocarbons
TLFD	two-level factorial design
TSDF	treatment, storage, and disposal facility
USAEC	U.S. Army Environmental Center
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet
V	volt
VOA	volatile organic analysis
VOC	volatile organic compound
VOST	volatile organic sampling train
w.c.	water column
W/m ²	watts per square meter

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1 INTRODUCTION

1.1 Background

The U.S. Army, U.S. Department of Energy, and U.S. Environmental Protection Agency (USEPA) initiated a joint program to develop a soil remediation system using concentrated solar energy. As a part of the program, the U.S. Army Environmental Center (USAEC) awarded a contract to Science Applications International Corporation (SAIC) for the development of a pilot-scale solar system effective in the treatment of hazardous wastes extracted from soils. The conceptual and detailed design of the system was completed under Tasks 1 and 2 of the program. Under Task 3, fabrication and demonstration testing of the pilot-scale system were accomplished. This document presents the results obtained during the Task 3 demonstration test.

1.2 Purpose and Scope

The purpose of this demonstration test was to evaluate the use of solar energy to thermally detoxify organic compounds removed from contaminated media by *ex situ* (such as thermal desorption) or *in situ* (such as soil vapor extraction) treatment systems, or desorbed from pretreatment matrices (such as activated carbon). Extraction systems are commercially available so the step of directly extracting organics from contaminated soil was excluded from the pilot-scale demonstration. Rather, the pilot-scale demonstration test focused on evaluating ultraviolet (UV)-rich solar destruction of volatile organic compounds (VOCs)¹ and semivolatile organic compounds (SVOCs)² by a solar incinerator and the environmental control of the resulting off-gases.

1.3 Goals and Objectives

The goal of the solar detoxification project was to demonstrate that solar energy could effectively treat hazardous wastes that are typically found in contaminated soils. The demonstration was designed to characterize reactor performance and to identify optimal operating conditions.

The pilot-scale demonstration test processed approximately 200 gallons of a surrogate waste mixture containing VOCs and SVOCs representative of soil contamination commonly found at U.S. Army remediation sites. During the demonstration, measurements were taken to determine the destruction efficiency (DE) for principal organic hazardous constituents (POHCs); the formation of products of incomplete combustion (PICs) [for example, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins/polychlorinated dibenzofurans (also known as dioxins/furans, or PCDDs/PCDFs)]; the production of criteria pollutants, including oxides of nitrogen (NO_x) and carbon monoxide (CO); and the emission of hydrochloric acid

¹ VOCs are organic compounds with boiling points below 100°C (212°F).

² SVOCs are organic compounds with boiling points above 100°C (212°F).

(HCl) from the scrubber. These measurements along with other data were used to characterize the performance of the solar reactor system. The specific objectives were to:

- Demonstrate the operation of a dish-mounted solar waste treatment system and identify optimal operating conditions for the process.
- Achieve DE³ of POHCs that meet or exceed the Resource Conservation and Recovery Act (RCRA) requirement of 99.99 percent for all POHCs in the waste feed.
- Achieve levels of PICs that are at or below levels typically emitted from hazardous waste incinerators.
- Meet or exceed the proposed hazardous waste combustion standards for 2,3,7,8-tetrachlorodibenzo(p)dioxin (2,3,7,8-TCDD) toxic equivalent (TEQ)⁴.
- Meet or exceed hazardous waste combustion standards for total hydrocarbons (THC) and CO emissions of 10 parts per million by volume (ppmv) and 100 ppmv, respectively.
- Generate lower NO_x emissions than conventional processing technologies⁵.
- Ensure HCl emissions from the exhaust scrubbing system meet the regulatory standards of 50 ppmv (dry, 7 percent O₂).

Additional information on these objectives, and the solar reactor's performance against them, are discussed in Section 6 of this report.

1.4 Roles and Responsibilities

SAIC served as designer, provider, and operator of the required solar concentrator for the design, fabrication, and testing under this program. Energy and Environmental Research Corporation (EER) supported SAIC, through subcontract, to provide expertise in the areas of incinerator design, operation, and data analysis. SAIC and EER functioned as an integrated team throughout this solar technology program and shared responsibility for the demonstration test. The organization responsibilities during the demonstration test are illustrated in Figure 1-1.

³ Destruction and removal efficiency (DRE) is used to measure the effectiveness of RCRA permitted waste treatment processes. Results are typically presented as DRE when the overall performance includes thermal destruction of toxic organics in the reactor and removal of trace residuals using a pollution control device. Because the solar detoxification system flue gas emission were measured upstream of the pollution control device (see Section 2), the performance is characterized as DE, rather than DRE

⁴ The proposed standard is 0.2 nanogram per dry standard cubic meter (ng/dscm) (dry, 7 percent O₂), but the promulgated standard may be increased to 0.4 ng/dscm (dry, 7 percent O₂).

⁵ Incinerators are not specifically required to meet a standard for NO_x emissions unless the area has been designated a nonattainment area under the Clean Air Act (CAA). The NO_x emissions of the solar reactor can be compared to the proposed medical waste standard of 210 ppmv (dry, 7 percent O₂) and municipal waste New Source Performance Standard (NSPS) of 180 ppmv (dry, 7 percent O₂).

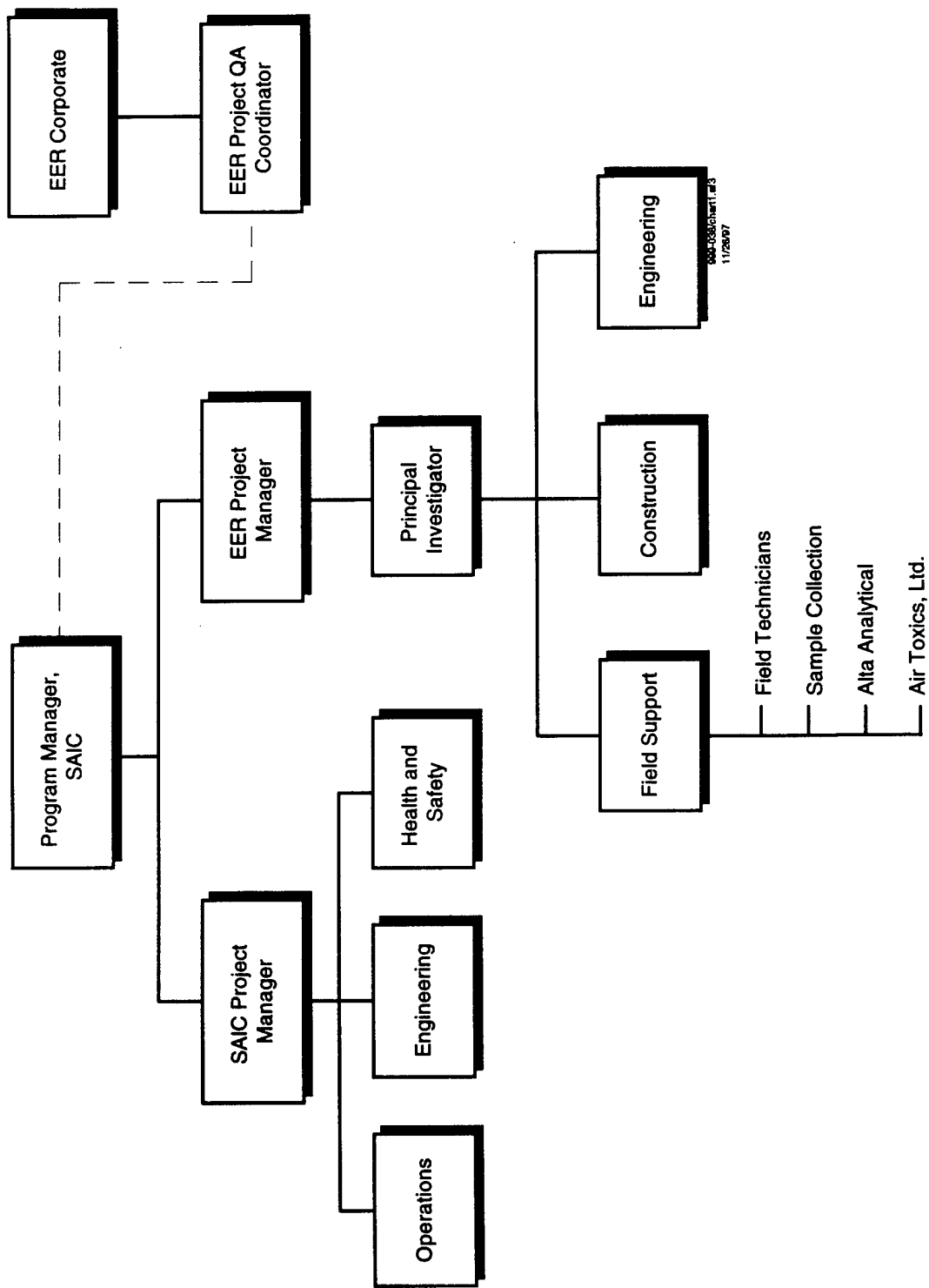


Figure 1-1. Demonstration Test Organization Responsibilities

1.5 Document Organization

The remaining sections of this document detail the solar technology demonstration test conducted during June of 1997. Section 2, Technology Description, provides a brief narrative description of solar technology and general comparison of the technology to classical incineration. This section also provides a brief description of the potential for solar insolation to improve overall performance of thermal processes such as incineration. A detailed description of the solar detoxification system employed during the demonstration test, and its subsystems, are also presented.

Section 3, Field Demonstration Testing, describes the conditions under which the demonstration test was performed. The test site is described, and the general test design parameters and operation variables are provided. The specific chemicals selected for processing during the test, known as a surrogate waste stream, are delineated and the basis for their selection is discussed. This section also describes site activities conducted during the test. Site regulatory requirements and site closure, including decontamination and decommissioning of the solar detoxification system and disposal of residual wastes, are also described in this section.

Section 4, Sampling Techniques and Analytical Methods, describes sampling locations, data requirements, sampling and analytical methods, and calibration procedures that were used to document performance against analytical test objectives.

Section 5, Quality, discusses the quality assurance (QA), quality control (QC), and data quality objectives (DQOs) that were enforced throughout the demonstration test.

Section 6, Technology Demonstration Results and Evaluation, provides a detailed discussion of the analytical results and DEs obtained, and analyzes the results against the detailed demonstration objectives. Included are evaluation of the solar concentrator, surrogate waste subsystem, solar reactor, and total system performance. Data quality achieved is also described. Based on these results, suggestions are made for future modifications that may enhance the system's operation and efficiency. The performance of the solar detoxification system is also compared to other technologies for destruction of organic wastes, and the economic factors of the technology are analyzed.

Section 7, Conclusions and Recommendations, provides an overall assessment of the system performance, summarizing the conclusions of the demonstration test against the specific test objectives. The conclusions are then used to develop recommendations for design changes and additional studies to enhance reactor performance.

2 TECHNOLOGY DESCRIPTION

2.1 Introduction

Although traditional incineration systems are highly efficient for the destruction of broad classes of organic chemicals, several aspects of the primary incinerator subsystem performance could benefit from improvement. These include the DE for waste feed organics, formation of PICs, such as PCDD and PCDF, and emission of criteria pollutants such as NO_x . Traditional incinerator systems typically treat exhaust gases from the primary incinerator with a secondary afterburner, heat removal system, and pollution abatement system to increase DE, reduce levels of PICs, and control criteria pollutant levels.

The solar detoxification system developed for this project employs a novel solar collector and reactor to assist the primary incineration process through thermal decomposition and photoactivation of organics. Similar to traditional incinerator systems, the solar detoxification system uses waste preparation and feed, heat removal, and pollution abatement elements to feed waste to the solar reactor and treat the reactor flue gases prior to their release to the atmosphere.

In the following paragraphs, the scientific basis for destruction of organic waste using incineration coupled with solar insolation is briefly discussed. The specific equipment used for the demonstration testing of this technology is then presented.

2.2 Solar Detoxification Process

The solar detoxification process is designed to increase the DE of the incineration process by using intense solar radiation to activate waste compounds and combustion products for further chemical reaction.

In a typical liquid incinerator, waste destruction takes place in a diffusion flame sustained by mixing atomized liquid waste with air in a burner nozzle assembly. Through a complex series of fast gas-phase chemical reactions, the vast majority of waste molecules fed into the flame are rapidly converted to other chemical species in the flame hot zone. Limitations common to all incinerators result in a very small fraction of waste molecules escaping destruction. In addition, a variety of VOCs, SVOCs [including PCDDs (dioxins) and PCDFs (furans)], and criteria pollutants are formed as combustion products. A secondary treatment is typically employed to further reduce the concentration of residual waste compounds, VOCs, and SVOCs in the exhaust gases prior to treatment in a pollution abatement system.

Solar treatment has been proposed as an alternative to classical incineration using a solar detoxification system. In the solar detoxification system, the incinerator diffusion flame and exhaust gases immediately downstream of the flame are exposed to intense solar radiation. Chemical compounds capable of absorbing the sunlight become more chemically reactive, further reducing their concentration through chemical reaction.

Organic chemicals that absorb light energy in the near UV and short wavelength portion of the visible spectrum can reach excited electronic states that require much less activation energy for chemical reaction (as noted in J.L. Graham and B. Dellinger, "Thermal/Photolytic Destruction of Hazardous Organic Wastes," *Energy* V 12, No. 3/4, pp 303-310, 1987). Since the absorption bands of organic compounds shift by as much as 200 nanometers (nm) toward longer wavelengths when the compounds are heated to incinerator temperatures, compounds with characteristic absorption maxima below 290 nm⁶ at room temperature may have a significant solar enhancement of destruction rate. Classes of compounds with these characteristics include aromatics and unsaturated organics commonly found as environmental contaminants and typically observed as chemical intermediates in flames.

Important parameters governing DE in the solar detoxification process are temperature, residence time, and turbulence in the solar reactor subsystem. In the solar reactor, flame temperatures are close to those in a normal thermal incinerator; however, the exhaust gas exit temperature from the diffusion flame is significantly lower in the solar reactor system due to cooling processes. Thus the overall temperature is significantly lower in the solar detoxification system. In addition, due to decreased air flow in the solar reactor system, the residence time is significantly greater in the solar reactor than in normal thermal incinerators. The increased residence time provides the additional time needed for the solar induced reactions to take place. The degree of turbulence is approximately the same in both technologies. Based on these considerations, the DE of the solar detoxification process is anticipated to be equal to or better than a classical hazardous waste incinerator.

2.3 Solar Detoxification System Description

The solar detoxification system designed for this demonstration is composed of five major integrated subsystems: a surrogate waste storage subsystem (SWSS), a solar concentrator subsystem, a solar reactor subsystem, a sample collection subsystem, and an exhaust gas subsystem. Figure 2-1 depicts the system, and the following paragraphs provide detailed descriptions of each subsystem.

2.3.1 Surrogate Waste Storage Subsystem

The SWSS stores liquid waste and feeds it to the solar reactor. The SWSS is composed of a vertical, 200-gallon, 316 stainless steel (SS) pressure vessel, including an in-tank mixer, a vapor recovery process, and a diaphragm pump [capacity of 11 gallons per minute (gpm)] as shown in Figure 2-2. The surrogate organic liquids used for testing, as described in Paragraph 3.4, are pumped from chemical containers into the pressure vessel with the air diaphragm pump. A scale is used to weigh each container before the organic liquid is pumped into the storage vessel. A liquid sight gauge, attached to the storage vessel, indicates liquid level. A vapor recovery process is included to eliminate the emission of VOCs to the atmosphere and the buildup of combustible gases. A 1/2-horsepower (hp) progressive cavity Moyno pump is used to deliver the liquid organic wastes from the storage vessel to the solar reactor. This pump is capable of delivering a discharge pressure of 100 pounds per square inch gauge (psig) at a flow rate of up to 4 gallons per hour (gph) to the solar reactor chamber.

⁶ 290 nm is the cutoff wavelength for transmission of ultraviolet light through air.

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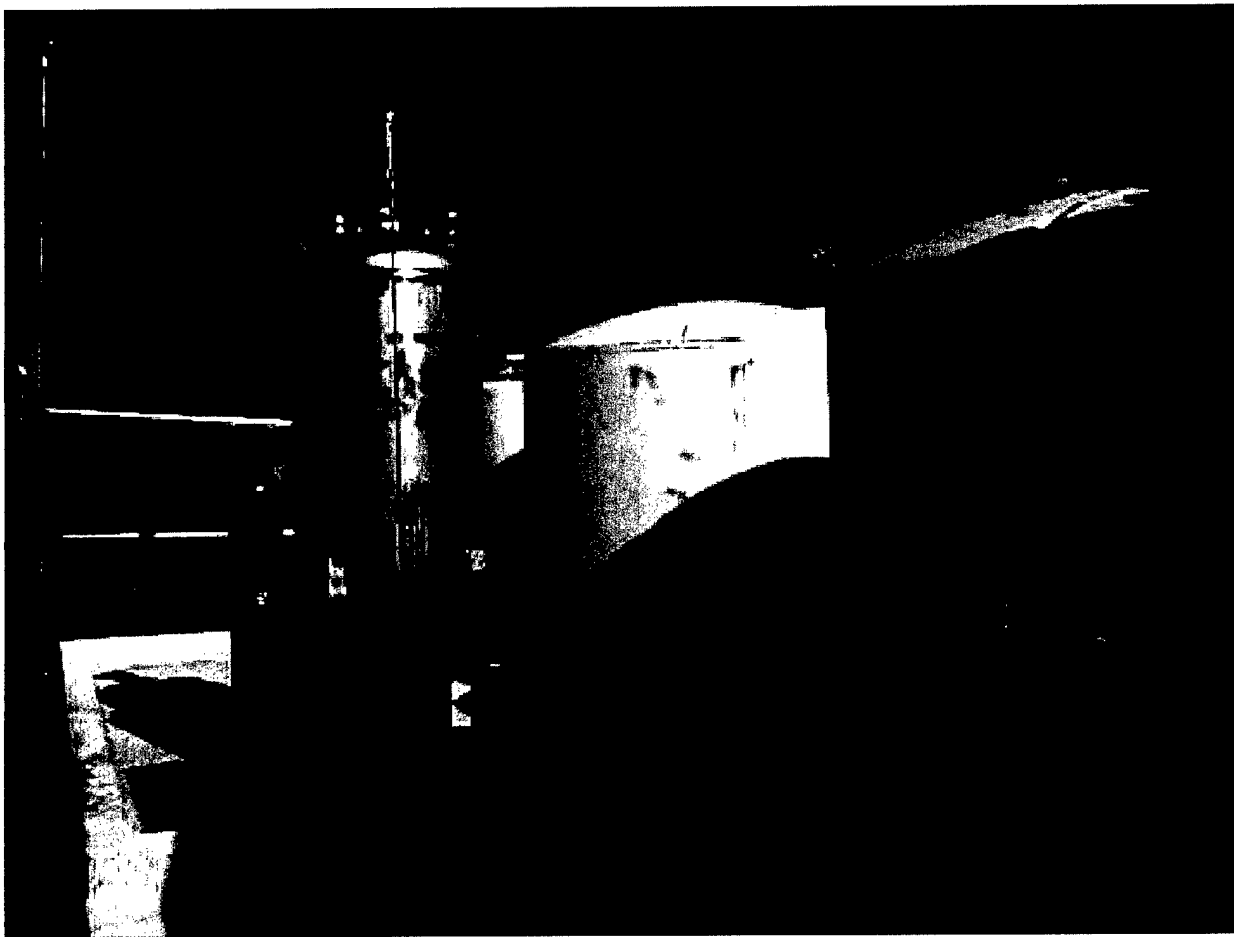


Figure 2-2. Surrogate Waste Storage Subsystem

2.3.2 Solar Concentrator Subsystem

The solar concentrator subsystem concentrates and focuses UV-rich solar radiation into the combustion chamber of the solar reactor subsystem (Paragraph 2.3.3). The solar concentrator is a faceted, stretched-membrane design developed for solar thermal applications, as shown in Figure 2-3. The solar dish concentrator specifications for this project are presented in Table 2-1.

As shown in Figure 2-3, the structure that supports the solar facets consists of radial trusses joined by circumferential trusses. The radial and circumferential trusses provide the mounting points for the 16 facets. The radial trusses converge to a hub assembly at the center of the dish. Projecting along the dish axis from the hub is a square, built-up interface that connects the dish to the drive unit. The drive unit is an elevation over azimuth gear drive with a torque tube connection to the dish. The dish facets are formed of rolled steel sections welded into rings. SS membranes (0.003-inch thick) are stretched over each side of the ring and welded to it. An aluminized polymer reflective film is laminated over the silvered glass surface of each facet to provide a highly UV-reflective surface. The optical focus of each facet is adjusted by drawing a slight vacuum in the plenum formed by the ring and membranes. The applied vacuum pulls the membranes into a concave shape resembling a parabola. The focus of each facet is individually controlled via a focus control valve assembly mounted through a hole in the ring.

A programmable logic controller (PLC) provides control of the solar dish concentrator, including tracking and operation of the focus control system. The PLC calculates the sun position based on the known location, date, and time of day, and positions the concentrator using an open-loop approach. Focus control for the dish is provided by a central vacuum blower. The blower is connected, via a manifold, to each of the facet focus control valves. To focus the dish, the blower is simply turned on, and each of the facet focus control valves modulate to control their focus. To defocus, the blower is turned off and the facets leak back to a defocused condition over a period of 3 to 5 minutes.

The PLC has a solar insolation monitor and wind sensor to provide inputs for system operation. The solar sensor is mounted along the dish axis, measuring direct solar insolation. The PLC has an insolation setpoint below which it defocuses the dish. The wind sensor is used to initiate a high wind stow; in this case, the dish is defocused and rotated to face upward (zenith stow) to reduce the loads on the drive unit. The system also includes limit switches that prevent over travel in either direction of azimuth and elevation. Reference switches are used to define the home position for the concentrator.

2.3.3 Solar Reactor Subsystem

The solar reactor subsystem is composed of a secondary optical element (SOE) and a solar reactor combustion chamber. The SOE and solar reactor combustion chamber are mounted to the boom of the dish array structure at the focal point of the solar concentrator. The flue gas quench unit is also located on the boom.

The SOE is a 2-foot long, water-cooled steel cone with a reflective inner surface that functions to homogenize the solar flux, reduce hot spots, and to increase the average flux within the length of

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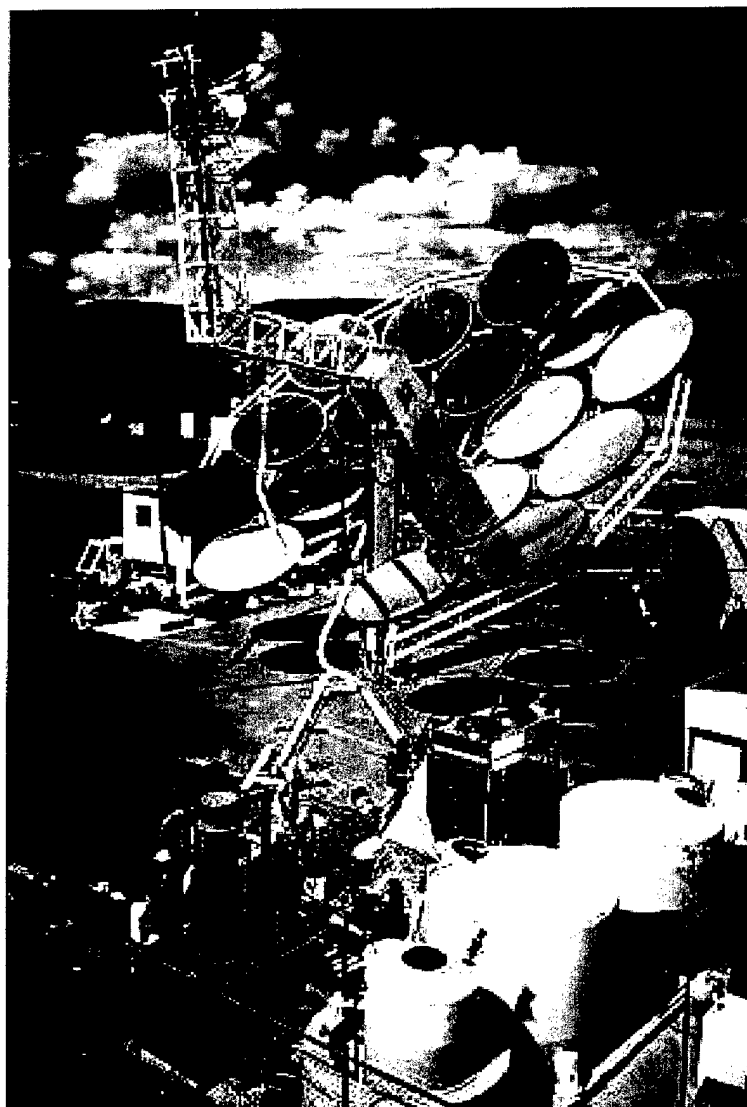


Figure 2-3. Solar Concentrator

Table 2-1. Solar Concentrator Specifications

<i>Type of Concentrator:</i>	Faceted stretched-membrane	<i>Total Area:</i>	93.0 square meters
<i>Drive Type:</i>	Elevation over azimuth, gear drive	<i>Projected Area:</i>	90.2 square meters
<i>Concentrator Structure:</i>	Radial/circumferential truss	<i>Number of Facets:</i>	16
<i>Nominal Focal Length:</i>	10 meters from dish vertex	<i>Facet Diameter:</i>	2.8 meters
<i>Reflector Film Reflectance:</i>	86% full spectrum	<i>Facet Slope Error:</i>	<2.5 milliradian

the solar reactor. It is mounted in front of the 18-inch diameter, 1/2-inch thick quartz window that allows passage of UV-rich solar energy into the reactor chamber.

The solar reactor is a 5-foot 4-inch high, water-cooled and refractory-lined vessel designed to enhance the solar destruction of the VOCs as shown in Figure 2-4. The reactor permits the evaluation of the nonthermal UV solar effect on waste destruction by providing a maximum solar thermal heat input of 200,000 British thermal units per hour (Btu/hr), also referred to as 200 thousand British thermal units per hour (kBtu/hr), during on-sun operations. Combined with the design waste heat input of 200 kBtu/hr, a maximum design heat input of 400 kBtu/hr can be achieved during on-sun waste destruction operations. The reactor is also designed to provide for a uniform temperature profile with a minimum gas residence time of 1 second. Table 2-2 shows the basic design criteria for the solar reactor.

During waste destruction operations, liquid surrogate waste is pumped to the solar reactor via the SWSS. A waste fuel injection process is used to atomize the liquid surrogate waste through a dual fluid air/liquid atomizing nozzle. From the compressed air line, atomizing air is introduced with the atomized liquid at a rate to maintain the desired reactor chamber temperature. A 4.5-hp Fuji regenerative blower is used to provide up to 100 standard cubic feet per minute (scfm) of combustion air to the reactor chamber.

Solar Reactor Subsystem Modifications. During initial testing of the system, it became apparent that the chemical heat input of 200 kBtu/hr provided by feeding the surrogate waste to the burner would not produce a stabilized flame. The quenching effect of the water-cooled wall around the nozzle destabilized the liquid injection flame, causing it to blow off the nozzle. In response to this problem, hot wall refractory was used to replace water cooling around the burner adaption section in the first 9 inches of the solar reactor. This modification affected only 4 percent of the water-cooled surface area and did not significantly impact operating temperatures.

Initial testing identified that, contrary to the original design, the solar reactor would not operate in a stable mode without the liquefied petroleum gas (LPG) pilot flame continuously providing approximately 30 kBtu/hr thermal input. To assure flame stabilization during the remainder of the testing, the LPG pilot flame was used in addition to the hot wall refractory modification to the entrance region of the reactor. The pilot flame was used to bring the reactor up to operating temperature and to provide localized heating near the liquid burner to ensure that the surrogate waste flame remained attached to the nozzle. Because the pilot flame burned separately from the liquid surrogate waste flame, it did not affect the chemistry of the surrogate waste flame

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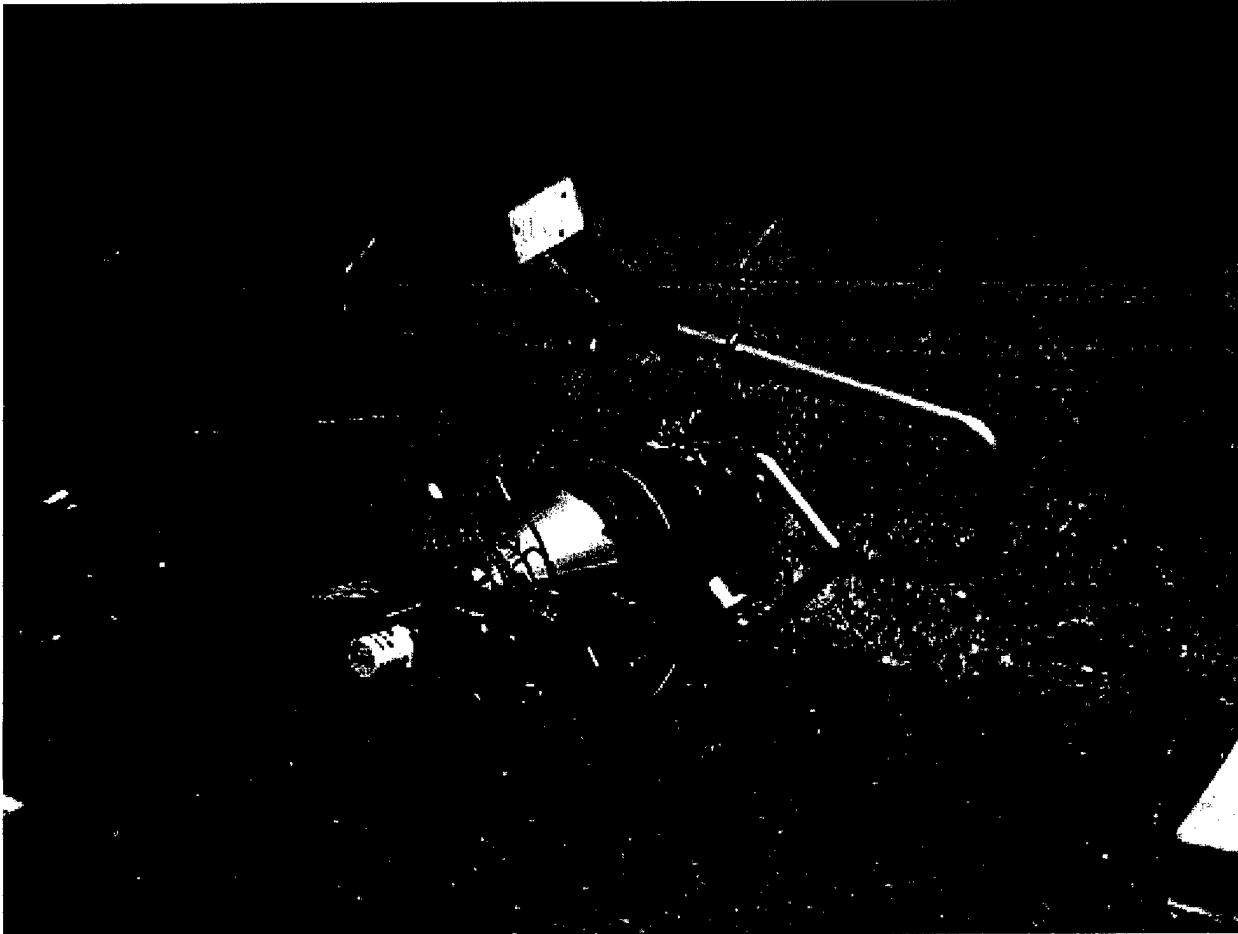


Figure 2-4. Solar Reactor

Table 2-2. Solar Reactor Design Criteria

<i>VOC Higher Heating Value:</i>	3,000 to 8,500 Btu/lb	<i>Solar to VOC Heat Input Ratio:</i>	1.0
<i>VOC Chlorine Content:</i>	57 to 80 wt%	<i>Reactor Solar Heat Flux:</i>	200,000 Btu/hr
<i>Solar Transmission Efficiencies:</i>		<i>Reactor Gas Temperature:</i>	700 to 1,000°C
• SOE	95%	<i>Reactor Gas Residence Time:</i>	1 second
• Quartz Window	90 to 95%	<i>Excess Combustion Air:</i>	100%
• Overall	86 to 90%	<i>Turndown Capability:</i>	3:1

Notes:

Btu/hr	=	British thermal units per hour
Btu/lb	=	British thermal units per pound
SOE	=	secondary optical element
VOC	=	volatile organic compound
wt%	=	weight percent

significantly. The pilot flame accounted for 15 percent of the fuel (chemical) heat input (30 kBtu/hr) and only 7.5 percent of the total heat input to the reactor during on-sun operations. Although the addition of the 15 percent LPG heat decreased the overall ratio of chlorine (Cl₂) to hydrogen and carbon in the solar reactor, the decrease was the same for both on-sun and off-sun operating waste destruction operations. Therefore, all conditions for determining the benefit of solar thermal input to the waste destruction process were comparable for on-sun and off-sun operations.

2.3.4 Sample Collection Subsystem

The sample collection subsystem provides for the collection of analytical samples needed to demonstrate the efficacy of the solar detoxification process. Sample locations are selected to ensure the samples obtained are representative of the surrogate waste feed and flue gas exhaust streams. A schematic of the process and the surrogate waste feed and flue gas sample locations are illustrated in Figure 2-5. The surrogate waste sample location is identified as WS1. The waste sample is collected through a 1/2-inch tubing nipple attached to the waste storage tank.

As shown in Figure 2-5, the flue gas sample ports are located both upstream and downstream of the venturi scrubber. The upstream and downstream flue gas sample locations are labeled FG1 and FG2 respectively. Continuous Emission Monitoring System (CEMS) measurements of flue gas composition [O₂, CO, carbon dioxide (CO₂), NO_x, and THC] are conducted at the upstream sample location (FG1). Continuous measurement of HCl emissions is performed downstream of the scrubber at sample location FG2. Manual method sampling for VOCs, SVOCs, and PCDDs/PCDFs is conducted upstream of the venturi scrubber (FG1). The upstream sample ports for CEMS and manual method samplings are located in the horizontal flue gas duct section between the flue gas humidification chamber and the venturi scrubber. This section of flue gas duct is constructed of 3-inch pipe.

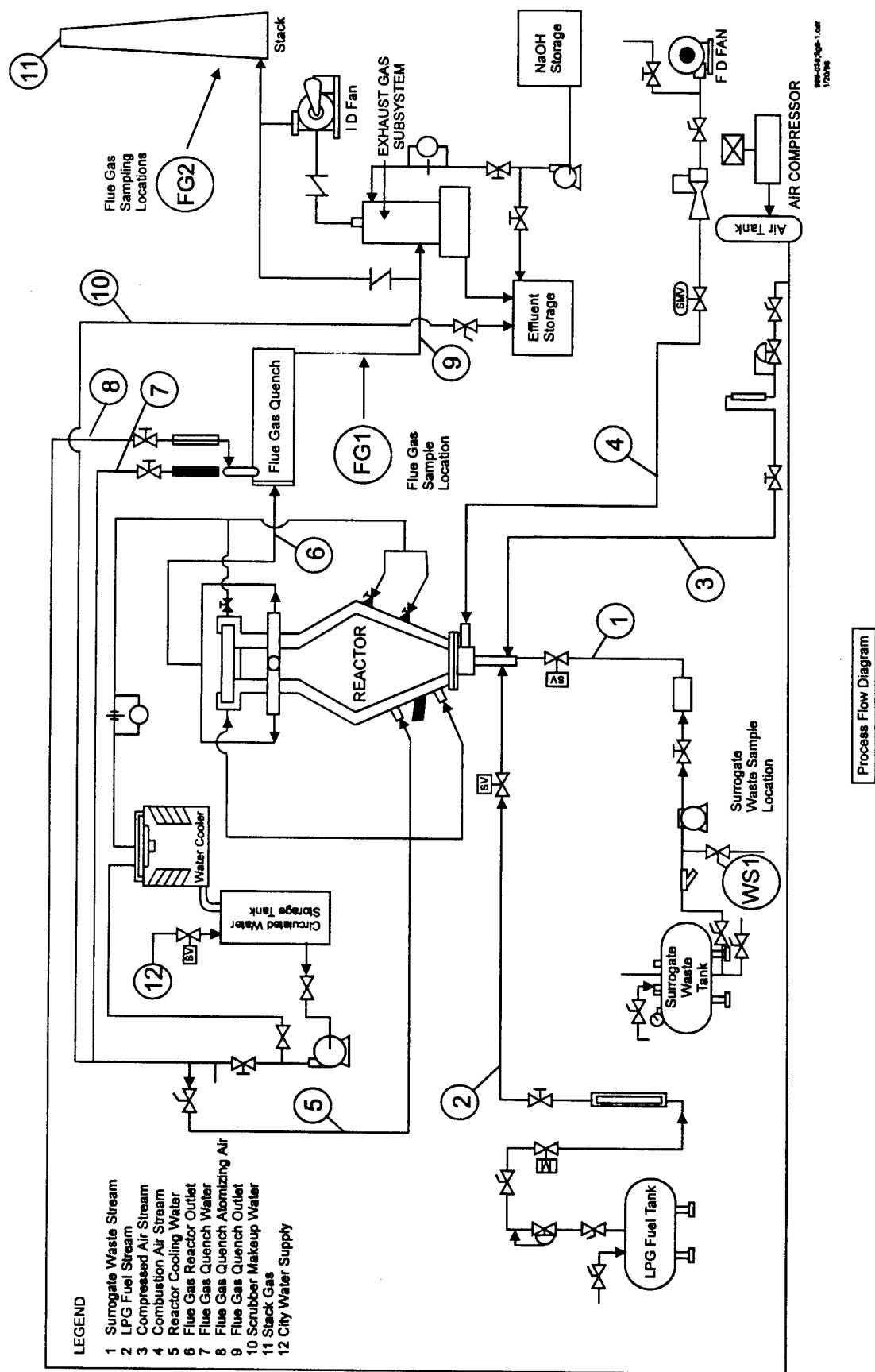


Figure 2-5. Process Flow Diagram and Sampling Locations

Figure 2-6 is a schematic of the sampling section of the flue gas duct. A total of six sample ports are contained in the flue gas duct so multiple samples can be collected simultaneously. The first port is used for CEMS measurements, the third port for VOC measurements, and the fifth port for SVOC measurements. The CEMS probe is located upstream of the manual method ports so that dilution air during manual method probe insertion does not impact CEMS measurements. The CEMS probe is constructed of 3/8-inch outside diameter (OD) SS tube. The manual method sample ports are separated by a minimum of 36 inches to allow required distance for flow stabilization between ports and to allow adequate room for sample equipment and personnel. The VOC and SVOC ports are equipped with 3/4-inch and 1-inch Swagelok[®] fittings, respectively, to prevent leakage of ambient air around the SS sample probes that sheath the quartz sample probes.

2.3.5 Exhaust Gas Subsystem

The exhaust gas subsystem cools the exhaust gases, maintains the exhaust temperature to the sample collection point to meet demonstration sampling requirements, and scrubs the exhaust gases to meet regulatory air emission requirements. The exhaust gas subsystem is composed of a quench vessel, venturi scrubber, waste sorbent storage tank, demister, induced draft (ID) fan, and stack.

The quench vessel, as shown in Figure 2-7, is located on the dish array boom in a position downstream of the solar reactor. It is used to cool the flue gas from the solar reactor using water evaporation cooling. Humidification water spray cools the gas to 240°C (470°F) to protect the downstream rotating swivel joints. The quench vessel has a dip leg that can drain into a sump located below the quench tank. From the quench vessel, the scrubber solution is recycled back to the quench spray nozzles and the downstream venturi and demister using a 3-hp corrosion-resistant recirculation pump. Cooled flue gas exits the quench vessel and flows through flexible hose and pipe to a downstream venturi scrubber located at ground level.

The venturi scrubber unit supplied by Global Concepts, Inc. is shown in Figure 2-8. Flue gas from the reactor quench vessel enters the scrubber spray quench tank made of AL6XN alloy where the flue gas is saturated with water⁷. Sodium hydroxide (NaOH) is added to the scrubber water to react with the HCl and Cl₂ to produce sodium chloride (NaCl) and sodium hypochlorite (NaOCl). The venturi scrubber is designed for 99 percent removal of HCl and Cl₂ and to limit particulate emissions to a level not greater than 0.03 grams (gr) per dry standard cubic feet (dscf) at 7 percent O₂. A purge stream (scrubber blow down) from the scrubber is designed to keep the concentration of the sodium-based salts within acceptable limits. The purged salt stream is stored in a waste sorbent storage tank for latter disposal at a municipal waste water treatment system.

⁷ All of the materials used for equipment and piping fabrication downstream of the quench tank are either fiber reinforced polyester (FRP) or chlorinated polyvinyl chloride (CPVC) plastic.

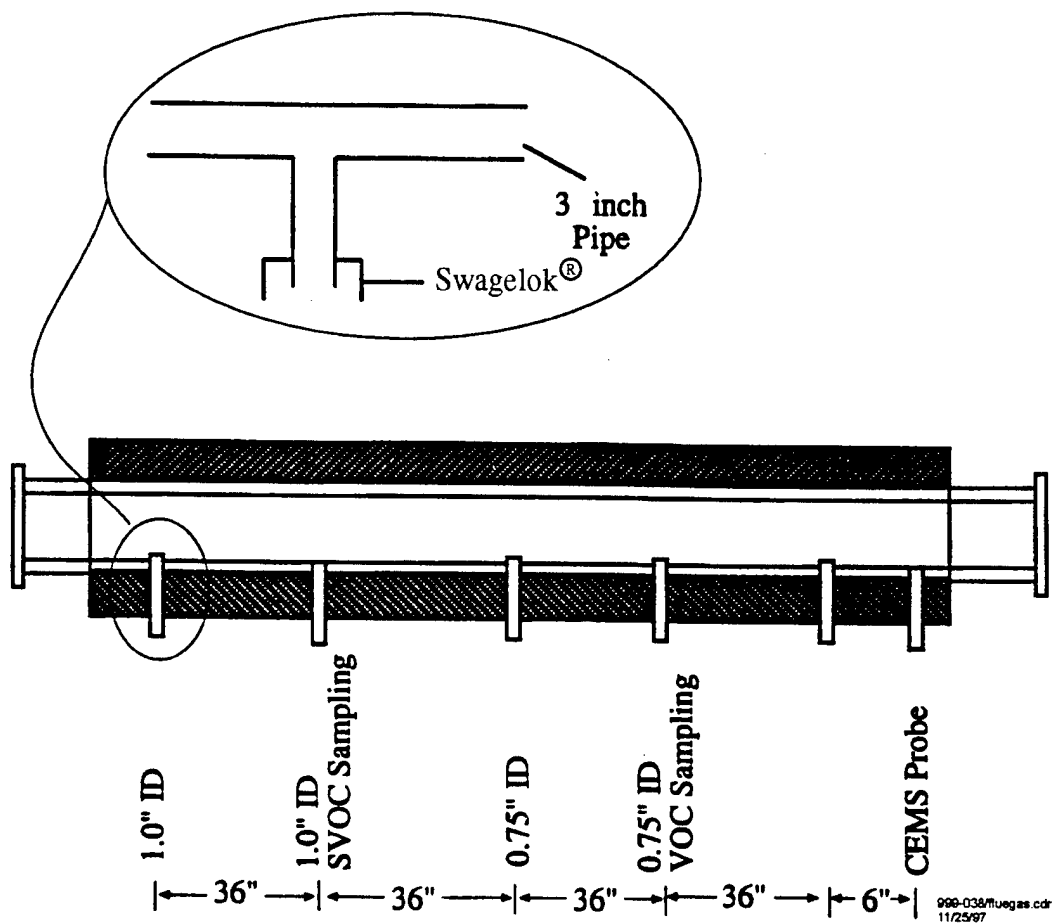


Figure 2-6. Upstream Flue Gas Sampling Section

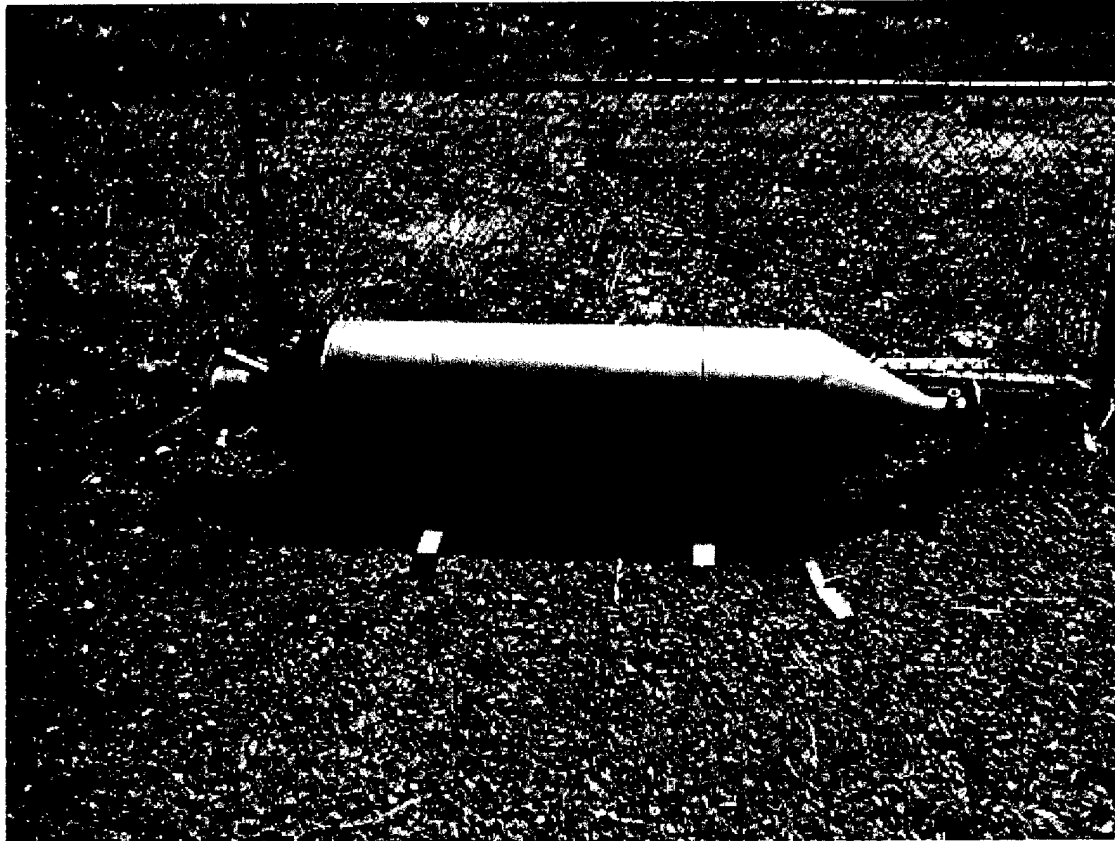


Figure 2-7. Quench Vessel



Figure 2-8. Scrubber Unit

The scrubbed flue gas from the venturi scrubber passes through a demister for fine solution droplet removal and then exits to the inlet of the ID fan. The ID fan provides the motive force to draw the flue gas from the reactor through the scrubber. From the ID fan, the treated flue gas exhausts through a stack to the atmosphere. A recycle line from the discharge of the ID fan flue gas to the inlet of the scrubber is used to maintain a constant negative pressure on the reactor system.

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3 FIELD DEMONSTRATION TESTING

3.1 Introduction

While abundant data exists for the effects of stoichiometry and waste feed rate on combustion processes, very little data had been collected on the optimal conditions for solar enhancement of waste destruction in an incinerator. Solar input was predicted to increase destruction of VOCs and SVOCs through radiant heating and UV decomposition. The field demonstration test conducted near Golden, Colorado, during the last 2 weeks of June 1997 was designed to broadly evaluate this solar effect and identify operating conditions leading to improved waste destruction. The following paragraphs describe the demonstration test, providing details of the demonstration test site, test design, surrogate waste characteristics, regulatory requirements for the test, daily test activities, and site closure.

3.2 Site Description

3.2.1 Site Layout and Facilities

The selected test site was located in Colorado between the cities of Golden and Boulder. Based on historical data, this site was projected to provide adequate sun intensities and duration during the June 1997 test period. The site was also determined to provide adequate space to accommodate the solar detoxification system and subsystems, support equipment, and facility requirements.

The general site layout is illustrated in Figure 3-1. The property, approximately 100 by 100 feet in area, was fully fenced with access through three gates. The solar concentrating dish and reactor were located in the center of the site. The concentrating dish and related systems required an area approximately 55 by 55 feet to accommodate the structure's movement required for sun tracking during the demonstration.

In the northeast corner of the site (Figure 3-1), a 23 by 25 foot concrete equipment pad provided a flat surface for the SWSS, process equipment, and the exhaust gas subsystem. Secondary containment for the SWSS, required to protect against chemical spills during handling and storage, was provided using a 6-inch high concrete curb around the SWSS boundary.

Two office trailers were utilized for the demonstration test, as illustrated in Figure 3-1. Because each trailer required approximately 30 by 10 feet for setup, access, and egress, they were located on opposite ends of the site.

- The first office trailer, 30 by 8 feet, was located on the north end of the site. This trailer was used during the demonstration to house the operating equipment (for example, computers and instrumentation) and personnel required to control the solar concentrating dish. The computers and instrumentation for reactor control and data acquisition were also located in this trailer.

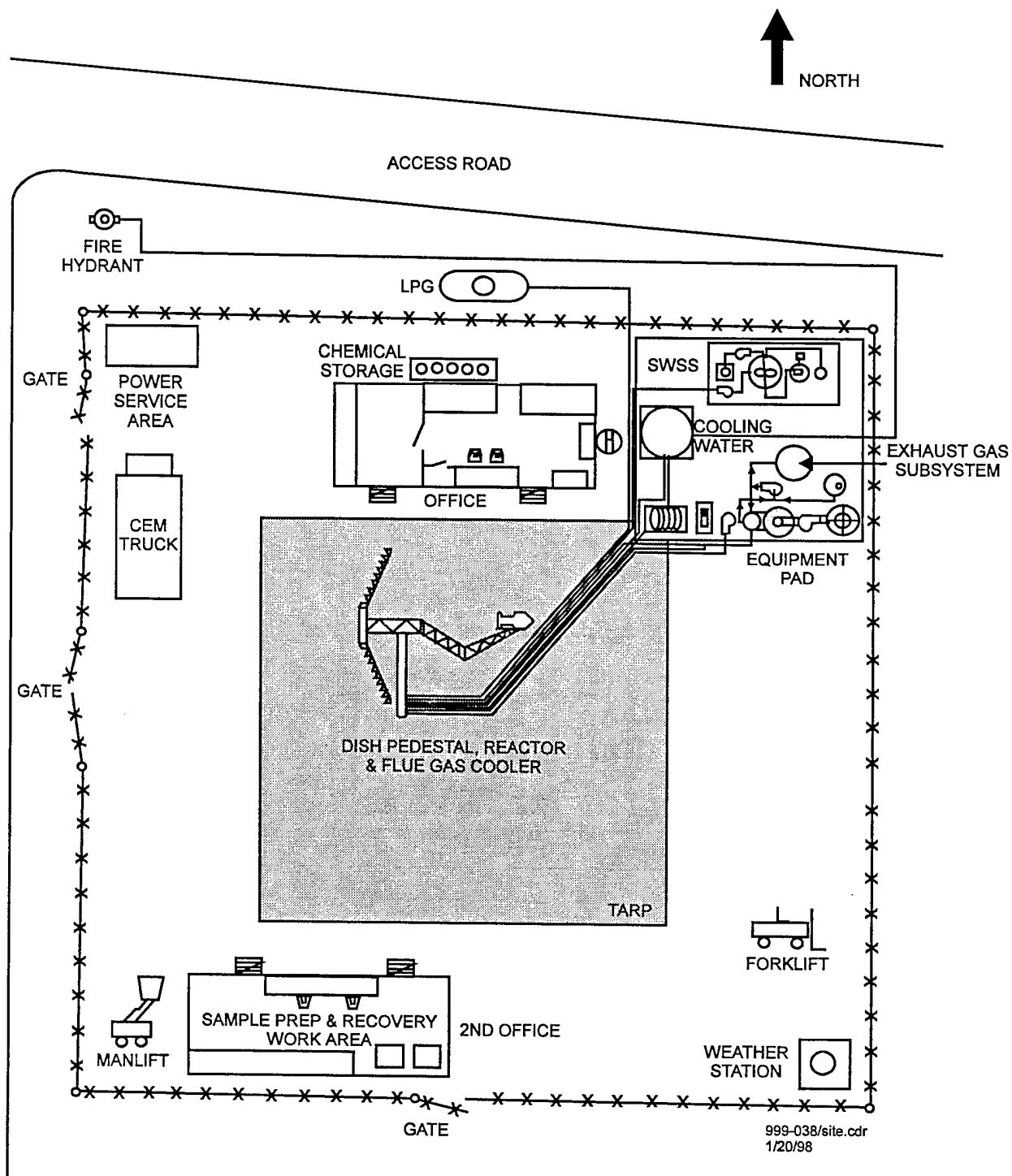


Figure 3-1. Site Layout for Demonstration Test

- A second office trailer, 40 by 8 feet, located on the south side of the site, provided a work area for manual method sample train preparation and recovery of VOCs, SVOCs, and PCDDs/PCDFs. CEMS equipment was located in a rental truck on the west side of the site.

A variety of support equipment and utilities was also available at the site, as indicated in Figure 3-1. At the northwest corner of the site, the power service area supplied 115/230/460-volt (V) electrical service; underground cable trenches among the power service area, office trailer, and dish provided power for control of the dish. Just north of the power service area, outside the fenceline, a fire hydrant equipped with a hose supplied water as needed. Also outside the northern fenceline, a 500-gallon tank provided LPG to the site. An air compressor was located on the east side of the first office trailer. Additional information regarding equipment, utilities, and consumables is described in the following paragraphs.

3.2.2 Test Equipment

Demonstration equipment, as detailed in Section 2, was available on-site throughout the test. A forklift, manlift, and safety equipment (for example, first-aid equipment, fire extinguishers, and chemical eyewash stations) were also available on-site to support the demonstration.

3.2.3 Utilities

Electrical power, compressed air, LPG, and cooling water were used to operate the solar concentrator and reactor.

3.2.3.1 Electrical Supply. The solar reactor operated at a minimum total electrical usage of 61 kilowatts (kW). This includes 460- and 230-V three-phase service and 220- and 110-V single-phase service. In addition, four 110V-20Amp circuits were required at the flue gas sample location upstream of the venturi scrubber. The specific equipment electrical requirements are presented in Table 3-1.

3.2.3.2 Compressed Air Supply. An air compressor capable of supplying 17.1 scfm at 175 psig of air was used. The compressor provided 10 scfm at 80 psig for atomizing airflow, and 5 to 7 scfm at 80 psig for operation of the scrubber air-activated valves.

3.2.3.3 City Water Supply. A city water source supplied water into a 1,100-gallon tank at the site on a daily basis. Approximately 540 gallons of water per day were required during operations, primarily to support the following processes:

- The reactor utilized up to 15 gpm of water flow for flue gas quench water.
- Make-up water for the scrubber was supplied directly from the city water source at a rate of between 1 and 2 gpm during waste firing operations.
- An emergency water hookup to the scrubber required a 30-gpm flow. This water was not used, but would have only been necessary for a short period in an emergency situation (that is, for a cooling water pump failure).

Table 3-1. Minimum Operating/Demonstration Electrical Requirements

Description	Voltage	Full Load Amps	Phase	Power (kW)
Cooling Water Circulating Pump	460	11	3	7.4
Air Compressor	460	8.3	3	5.6
Ring Blower	460	5.5	3	3.7
Scrubber	460	<u>12</u>	3	<u>8.1</u>
Total	—	36.8	—	24.8
Circulating Water Cooler	230	5.2	3	2.0
Surrogate Waste Pump	230	<u>1.1</u>	3	<u>0.4</u>
Total	—	6.3	—	2.4
Scrubber	110	10	1	1.6
Control Valves	110	3	1	0.5
Control Panel Signals	110	20	1	3.2
Control Panel Power	110	20	1	3.2
CEMS Rack	110	15	1	2.4
Field Sample Equipment	110	15	1	2.4
Field Sample Equipment	110	15	1	2.4
Field Sample Equipment	110	15	1	2.4
Swirl Actuator Motor	110	2	1	0.3
CEMS Sample Pumps	110	4	1	0.6
Heat Tapes	110	30	1	4.9
Chillers	110	<u>5</u>	1	<u>0.8</u>
Total	—	154	—	24.7
Field Crew Trailer	220	30	—	9.7
Total Power				61.6

Notes:

CEMS = Continuous Emission Monitoring System
kW = kilowatt

Reactor cooling water was recirculated and cooled in an indirect cooler; therefore, make-up reactor cooling water was not required.

3.2.3.4 LPG Fuel Supply. LPG was provided from a 500-gallon LPG tank located outside of the fence on the north side of the site. LPG was utilized to fire the reactor up to 200 kBtu/hr, requiring 80 scfh at 25 psig. The maximum daily LPG requirement was 800 standard cubic feet (scf).

During normal operation, the reactor startup on LPG ran for 1 to 4 hours daily at full load requiring 200 to 400 scf of LPG. During shakedown operation, the reactor operated for up to 10 hours at maximum load.

3.2.4 Consumables

A 540-gallon tank filled with 50 percent NaOH in solution was provided to neutralize the scrubber liquor pH during chlorinated waste feed operations. The maximum NaOH usage was 10 gph during waste feed. Over a typical 4-hour-per-day waste feed operation, 40 gallons of NaOH solution were used.

3.3 Test Design

Solar insolation effects on the destruction of VOCs and SVOCs were the focus of the demonstration. While abundant data exists for the effects of stoichiometry and waste feed on combustion processes, very little solar performance data are available to define the optimal conditions for waste destruction. Thermal modeling conducted during the design of the system indicated that solar insolation may have a significant effect on reactor temperature and slight effect on gas residence time. Solar insolation should also improve temperature uniformity in the reactor and alter heat transfer mechanisms to improve waste DE. Solar input was predicted to improve temperature uniformity, provide increased residence time, reduce auxiliary fuel usage during on-sun testing, and improve waste destruction by radiant heating and UV decomposition. The test design was selected to evaluate the solar effect and identify processing conditions where impacts are most significant.

3.3.1 Test Matrix

To meet the objectives of this demonstration, a two-level factorial design (TLFD) test matrix was originally developed to study the three process variables anticipated to have a primary effect on system performance. These factors were waste feed rate, stoichiometry [air to fuel (waste) ratio], and solar insolation. Waste feed rate and stoichiometry are important variables in conventional thermal systems for optimizing DEs. Solar insolation is a key variable for this demonstration because it indicates the viability of solar-assisted waste destruction. Due to time constraints caused by an accelerated project end date, weather problems, and equipment problems encountered during shakedown (see Paragraph 2.3.3), the test matrix was modified to evaluate the effect of variations in stoichiometry and solar input on system performance at constant chemical heat input (waste feed rate).

As shown in Table 3-2, the final test matrix varied the stoichiometry and solar input during the first four tests and then ran three replicate tests at average, or center point conditions. The final test repeated the conditions of the first test, which exhibited unusual particulate loading caused by the first full day of sun tracking. The final test matrix differed from the original by holding chemical heat input constant at the full load condition of 200 kBtu/hr, decreasing the range of stoichiometries from 1.50 to 2.65 down to 1.2 to 1.4 (20 to 40 percent excess air), and testing solar input at 100 kBtu/hr in addition to 0 kBtu/hr and the full design solar input of approximately 200 kBtu/hr. Constant chemical heat input was provided as approximately 30 kBtu/hr from the LPG pilot flame and 170 kBtu/hr from combustion of the surrogate waste feed.

Table 3-2. Final Two-Level Factorial Design Test Matrix

Test Condition	Heat Input (kBtu/hr) ^a	Stoichiometry	Solar Input (kBtu/hr)
1	200	1.2	200
2	200	1.2	0
3	200	1.4	200
4	200	1.4	0
5	200	1.3	100
6	200	1.3	100
7	200	1.3	100
8	200	1.2	200

Note:

kBtu/hr = thousand British thermal units per hour

^a Heat input from the LPG pilot flame and combustion of the surrogate waste feed

None of these changes impacted the ability to achieve the demonstration objectives. The final test matrix provided the basis for evaluating solar reactor performance against Federal regulatory standards for POHC DEs; low levels of PICs and NO_x; formation of PCDD/PCDF; and THC and CO emissions. Comparison of data from on-sun versus off-sun waste treatment tests also supports the evaluation of the solar effect in the incineration process.

3.3.2 Test Parameters and Variables

3.3.2.1 Variable Operating Parameters. The reactor was tested over a range of stoichiometries that were controlled by varying the secondary combustion air input into the reactor at a constant chemical heat input as shown in Table 3-3. Stoichiometries were varied from 1.2 to 1.4 by varying secondary combustion air flow rates from 32 to 37 scfm. Waste feed and primary combustion atomizing air for waste atomization were maintained at 1.55 gph and 3.5 scfm, respectively.

The reactor was also tested with varying levels of insolation supplied by the solar dish array. Insolation was varied from full input to 0 input by taking facets out of service (defocusing). The nominal insolation into the reactor was 0, 100, and 200 kBtu/hr. The solar dish was operated without on-sun tracking and with on-sun tracking with 8 facets or 16 facets focused to achieve the low, middle, and high insolation levels. Solar flux was measured during tests using a dish-mounted normal incidence pyrheliometer (NIP) to ensure good solar conditions.

The cloudy weather in Golden, Colorado, during the month of June effected the solar insolation, with occasional clouds of varying density passing between the sun and the dish during test periods. In some instances, sampling was stopped for several minutes while the cloud moved away and the reactor came back to temperature. In other cases, testing was rescheduled for another day. Because the reactor operated between 0 and 200 kBtu/hr solar input extremes, the

Table 3-3. Test Variables

Test No.	Variable Operating Parameters			Constant Operating Parameters				
	Solar (kBtu/hr)	Stoich.	Sec. Air (scfm)	Prim. Air (scfm)	Waste (gph)	LPG Pilot (kBtu/hr)	Swirl (degrees rotation)	Pressure (inches w.c.)
1	200	1.2	32	3.5	1.55	30	40 to 45	-10
2	0	1.2	32	3.5	1.55	30	40 to 45	-10
3	200	1.4	38	3.5	1.55	30	40 to 45	-10
4	0	1.4	38	3.5	1.55	30	40 to 45	-10
5	0	1.4	38	3.5	1.55	30	40 to 45	-10
6	100	1.3	35	3.5	1.55	30	40 to 45	-10
7	100	1.3	35	3.5	1.55	30	40 to 45	-10
8	100	1.3	35	3.5	1.55	30	40 to 45	-10
9	200	1.2	32	3.5	1.55	30	40 to 45	-10

Notes:

gph = gallons per hour
 inches w.c. = inches of water column
 kBtu/hr = thousand British thermal units per hour
 LPG = liquefied petroleum gas
 Prim. Air = primary combustion atomizing air
 scfh = standard cubic feet per hour
 scfm = standard cubic feet per minute
 Sec. Air = secondary combustion air input
 Stoich. = stoichiometry

small variation (less than 20 kBtu/hr) in insolation during on-sun tests was assumed to be relatively insignificant in changing the reactor's performance.

3.3.2.2 Constant Operating Parameters. Atomizing airflow rate was set at 3.5 scfm for reasonable atomization performance. Waste was fed at 1.55 gph corresponding to 170 kBtu/hr of chemical heat input. The LPG pilot flame was kept at 30 kBtu/hr heat input. To assist in stabilizing the flame, the burner combustion air swirl was kept at approximately 40 to 45 degrees in rotation. Swirl was measured by a position indicator on the swirl actuator drive and was generally repeatable to ± 2.5 degrees. Swirl variation is intrinsically part of the process variability.

The flue gas quench was operated with a liquid water injector with 3.5 scfm of atomizing air and a variable amount of water to control the gas temperature at the high temperature swivel to below 470°F. The flue gas scrubber was a turnkey system designed to control the reactor pressure between -12 and -5 inches water column (w.c.). The scrubber also provided automatic feed control of caustic to neutralize acids captured in the scrubber water. Neutralized scrubber water was discharged to the effluent water tank at a rate of between 1 and 2 gpm during HCl scrubbing operations.

3.3.2.3 Operating Responses. The operating responses recorded during testing included cooling water flow rate and inlet and outlet water temperature, reactor exit gas temperature, flue gas composition (CO₂, O₂, CO, NO_x, and THC), flue gas organics (VOCs and SVOCs), and stack gas HCl.

3.4 Surrogate Waste

The demonstration was designed to determine the efficacy of the solar reactor for treating wastes typically extracted from contaminated soils. To ensure the representativeness of the wastes being studied, a surrogate waste formulation was developed containing a variety of common soil contaminants at U.S. Army remediation sites and at other federal and industrial hazardous waste sites. Eight chemicals were selected to compose this surrogate waste stream:

- Six chemicals were selected based on their identification in the USAEC Installation Restoration Data Management Information System (IRDMIS) roster of 25 most common organic contaminants at Army remediation sites: 1,2-dichlorobenzene (1,2-DCB), trichloroethylene (TCE), benzene, ethylbenzene, toluene, and xylene (isomers of dimethylbenzene).

In practice, ineffective thermal treatment of these compounds leads to the formation of various PICs that are of particular interest because of their environmental and health impacts. Also, a photothermal effect has been demonstrated for each of these compounds (as noted in B. Dellinger, Presentation given at 1992 Tri-Agency Meeting), so they are optimal for demonstrating the potential for solar detoxification of soil contaminants. These compounds served as POHCs on which DEs were determined for the demonstration.

- In addition, carbon tetrachloride and pentachlorophenol (PCP) were selected to generate PCDD/PCDF during the treatment, allowing evaluation against the objective to meet or exceed the combustion standards for 2,3,7,8-TCDD TEQ. PCP is a common contaminant at Superfund sites, and is structurally similar to polychlorinated biphenyl (PCB), which produces PCDD/PCDF in conventional thermal technology emissions. PCB is banned for use in the United States, and the required waste feed volume necessary for the demonstration was not readily available. Therefore, PCP was used as a substitute.

1,2-DCB and TCE were selected as the primary constituents of the surrogate waste, each representing 25 percent by mass of the waste composition. Benzene, ethylbenzene, toluene, and xylene were added at 10 percent by mass and carbon tetrachloride and PCP added at 5 percent by mass. Table 3-4 shows the volume of each compound required per day and their physical properties. Table 3-5 shows the composition, physical properties, and feed rate for the surrogate waste during demonstration testing.

Table 3-4. Surrogate Waste Volume Requirements

Component	Lb/hr	Lb/day	Kg/day	Density kg/L	L/day
1,2-Dichlorobenzene (1,2-DCB)	4.85	19.40	8.80	1.3059	6.74
Trichloroethylene (TCE)	4.85	19.40	8.80	1.4642	6.01
Benzene	1.94	7.76	3.52	0.8765	4.02
Ethylbenzene	1.94	7.76	3.52	0.8670	4.06
Toluene	1.94	7.76	3.52	0.8669	4.06
Xylene	1.94	7.76	3.52	0.8802	4.00
Pentachlorophenol (PCP)	0.97	3.88	1.76	1.9780	0.89
Carbon tetrachloride	0.97	3.88	1.76	1.5940	1.10
TOTAL	19.40	77.60	35.20	—	30.88

Notes:

kg/day = kilogram per day
kg/L = kilogram per liter
L/day = liter per day
lb/day = pound per day
lb/hr = pound per hour

3.5 Regulatory Requirements Applicable to Site Operations

3.5.1 General Requirements

Hazardous waste was not processed during the solar detoxification demonstration. Although the system was designed to handle hazardous waste, a decision was made to use a surrogate waste for this demonstration test; therefore, RCRA regulations were not applicable to the surrogate waste treatment process.

The surrogate waste was composed of pure organic compounds purchased directly from chemical supply companies. These chemicals were purchased in small containers and mixed on a daily basis, ensuring that unprocessed chemicals did not form a hazardous waste requiring disposition at the completion of the test. However, residual waste was generated following chemical processing in the solar reactor. Management of the residual wastes are described in the following paragraphs.

3.5.2 Residuals Management

As part of the normal operation of the solar reactor, low concentrations of the surrogate waste organic compounds were exhausted to the air, emitted in the scrubber waste effluent, and emitted to the air via the vapor recovery system. Projected estimates of the concentrations of these organic compounds were calculated and compared to the air and water emission standards as determined by the Colorado Department of Public Health and Environment (CDPHE). Disposal options were evaluated as described in the following paragraphs.

Table 3-5. Surrogate Waste Composition and Feed Rate

Chemical Constituent	Percentage, by Weight, in Surrogate Waste	Molecular Weight	Formula
1,2-Dichlorobenzene (1,2-DCB)	25.0	147	C ₆ H ₄ Cl ₂
Trichloroethylene (TCE)	25.0	131	C ₂ HCl ₃
Benzene	10.0	78	C ₆ H ₆
Ethylbenzene	10.0	106	C ₈ H ₁₀
Toluene	10.0	92.1	C ₇ H ₈
Xylene	10.0	106	C ₈ H ₁₀
Carbon Tetrachloride	5.0	154	CCl ₄
<u>Pentachlorophenol (PCP)</u>	<u>5.0</u>	266	C ₆ HCl ₅ O
Total	100.0	—	—

<u>Elemental Analysis</u>	<u>Percent by Volume</u>
Carbon	55.0
Hydrogen	4.4
Chlorine	40.3
<u>Oxygen</u>	<u>0.3</u>
Total	100.0

<u>Properties</u>	
Heating Value, Btu/lb	10.240
Specific Gravity	1.27
Air to Fuel (Waste) Ratio, lb/lb	7.19
Soluble in Water	No

<u>Waste Feed</u>	
Waste Heat Input, kBtu/hr	170
Waste Feed Rate, lb/hr	16.4
Waste Feed Rate, gph	1.55

Notes:

Btu/lb = British thermal units per pound
 gph = gallons per hour
 kBtu/hr = thousand British thermal units per hour
 lb/hr = pound per hour
 lb/lb = pound per pound

3.5.2.1 Air Emission Levels. Prior to the demonstration test, project air emission rates were calculated to be 0.2 pound per demonstration period assuming a 99.99 percent destruction rate and a total feed volume of 198 gallons. Individual emission rates were summed as a single point discharge. Based on this calculated emission rate, an air permit was obtained from CDPHE.

3.5.2.2 Scrubber Waste Effluent Emission Level. Liquid waste effluents were emitted from the scrubber at a rate of approximately 60 gph during the operation of the solar reactor (approximately 4 to 6 hours per day). Based on Sections 6.17 [6.13, 6.14] and 6.18 of the Metro District's Rules and Regulations, the scrubber waste effluent qualified for disposal into the sanitary sewer system if the pH was greater than 5.0 and the concentration of TCE was less than 1.5 parts per million (ppm).

A sample of the scrubber waste effluent was submitted to the laboratory for organic analysis to accurately determine TCE concentrations. Laboratory results indicated that the organic concentrations were below the detection limit for all chemicals other than 1,2-DCB and TCE, which were present at a maximum of 0.160 ppm and 0.025 ppm, respectively. The TCE level was well below the regulatory requirement for disposition as hazardous waste, and the scrubber effluent was discarded into the sanitary sewer system.

3.5.2.3 Vapor Recovery Effluent. Liquid waste effluent, composed of condensed VOCs and SVOCs, was emitted from the SWSS at a rate of approximately 0.1 gallon per day during the operation of the solar detoxification system (approximately 4 to 6 hours per day). The total volume of effluent requiring disposal was calculated to approximately 2 gallons. It was sent to a treatment, storage, and disposal facility (TSDF) for disposal as a hazardous waste.

3.6 Site Activities

3.6.1 Daily Operations

During the demonstration tests, early morning startup consisted of turning on the reactor and SOE cooling water pump and lowering the dish to maintenance position (reactor at ground level). The forced draft (FD) fan and air compressor were started. The FD fan was used to provide the main combustion air for the solar reactor. The scrubber was then started by turning the quench water pump on and powering up the ID fan. The scrubber reflux valve was adjusted to set reactor pressure at -10 inches w.c.

The reactor control system initiated an air purge of the reactor and then provided an LPG start permissive. The LPG heat-up flame was started at a rate of 150 kBtu/hr with a stoichiometry of 1.5. The LPG and airflow rate settings were set at 62 scfh and 35.5 scfm, respectively.

The firing rate was turned up to 200 kBtu/hr at the same airflow resulting in a stoichiometry of 1.08 for a more rapid heat-up time. After the downstream ducting temperatures met a minimum temperature of 121°C (250°F) at the scrubber, the LPG-to-waste switching was initiated. The heat-up time on LPG was approximately 1 hour.

Waste switching was done by turning the LPG to 125 kBtu/hr at a stoichiometry of 1.74. Waste input was then started by gradually increasing the waste firing rate to 100 kBtu/hr over approximately 2 minutes. Next, the LPG was reduced to 100 kBtu/hr and the waste was

increased proportionally. This switching process was continued until the waste was firing at 170 kBtu/hr with a stabilizing LPG pilot at 30 kBtu/hr. Air was adjusted to achieve the desired stoichiometry. The LPG pilot flame was left on to assist the waste flame stabilization as described in Paragraph 2.3.3. The dish was then permitted to track for on-sun tests. When waste was firing, the water blow-down rate from the scrubber was turned on. The water blow-down rate was approximately 1 to 2 gpm.

After the thermal conditions in the reactor were stabilized for a desired test condition, the manual method sampling was begun. While the reactor was in heat-up mode, the CEMS was calibrated with span and zero gases in direct and biased modes. Although the reactor was operated with minimal operator supervision, during testing operators continuously monitored and recorded operating points and settings to ensure the test condition was held constant.

After waste firing, the reactor was switched back to 100 percent LPG fuel to purge the high HCl (3 percent) concentrations in the flue gas. The switching process involved increasing LPG by 25 kBtu/hr, then reducing the waste by 25 kBtu/hr. LPG and waste were switched over repeatedly until the LPG reached at least 125 kBtu/hr. Then waste was turned off and LPG was increased to between 150 and 200 kBtu/hr. The reactor was run with LPG firing for at least 10 minutes to purge the HCl from the ducting.

Shutdown involved pressing the LPG stop button and waiting several minutes for the reactor to cool. The FD fan, scrubber, and air compressor were then turned off. Systems were shut down by closing manual shutoff valves to prevent discharges of LPG, water, and effluent in the event of a power failure.

A representative schedule showing typical daily operation activities is included as Table 3-6. Durations identified for specific activities, such as on-sun waste firing and testing, are approximations. Actual durations varied between test runs.

3.6.2 Sequence of Events

Nine tests were conducted during the month of June, 1997 as shown in Table 3-7. The tests included the eight sets of conditions listed in the TLFD test matrix shown in Table 3-2. Two tests were run to repeat the conditions of Tests 1 and 4. The eighth test was conducted as a repeat of the fourth test, which failed to achieve the test parameters due to a flame outage. The ninth test was conducted as a repeat of the first test, which had unusual particulate loading caused by the first full day of sun tracking.

3.7 Site Closure

Following the completion of the last test, most of the remaining surrogate waste was processed through the reactor.⁸ Next, the test equipment was decontaminated by flushing the SWSS, the reactor, and all lines connected to the system with diesel fuel. Diesel fuel was pumped into the SWSS storage tank, then fed to the reactor for combustion. By feeding diesel fuel through the system, all hazardous materials used during the demonstration were flushed from the system.

⁸ Due to time constraints, only a portion of the excess surrogate waste was processed.

Table 3-6. Examples of Typical Daily Operation Activities

Activities	Daily Hours															
	5:00	5:30	6:00	6:30	7:00	7:30	8:00	8:30	9:00	9:30	10:00	10:30	11:00	11:30	12:00	12:30
Solar Dish to Maintenance	■															
Systems Start-Up		■														
LPG Start-Up and Heat-Up			■	■	■	■										
LPG to Waste Switching				■	■	■	■									
Track to Sun					■	■	■	■	■	■	■	■	■	■	■	■
On-Sun Waste Firing							■	■	■	■	■	■	■	■	■	■
Testing										■	■	■	■	■	■	■
Waste to LPG Firing																■
Reactor and System Shutdown																■

Following decontamination of the test equipment, the Golden Test Site was returned to its predemonstration condition. Rental equipment, such as the field recovery trailer and forklift, was returned to the owners. All deliverable equipment and supplies were inventoried, packaged, and removed from the site in preparation for transfer to the Army. A list of the inventoried items was transmitted to USAEC and the items shipped to a location designated by USAEC.

Hazardous waste was not processed during the solar detoxification demonstration. Residual wastes generated during the demonstration test were managed as previously described in Paragraph 3.5.2.

All hazardous waste and contaminated materials accumulated during the demonstration were sent to the Highway 36 TSDF, including the remaining excess surrogate waste mixture remaining in the storage vessel, vapor recovery system effluent, and miscellaneous solid materials such as Tyvek and booms from the dish array structure. All other nonhazardous disposable equipment and supplies were transported to the Browning Ferris Industries (BFI) sanitary landfill on Highway 93.

Table 3-7. Summary Daily Testing Log

Test No.	Testing Date	Test Parameters	Sample Collection Time (minutes)	Test Parameters Satisfied? (Yes/No)	Comments/Unusual Conditions
1	06/20/97	<ul style="list-style-type: none"> • 200 kBtu/hr solar • 1.2 stoichiometry 	109	Yes	<ul style="list-style-type: none"> • SVOC sample train showed high particulate loading, first on-sun test in several days • Test flagged for possible repeat
2	06/20/97	<ul style="list-style-type: none"> • 0 kBtu/hr solar • 1.2 stoichiometry 	120	Yes	No problems encountered
3	06/21/97	<ul style="list-style-type: none"> • 200 kBtu/hr solar • 1.4 stoichiometry 	120	Yes	No problems encountered
4	06/21/97	<ul style="list-style-type: none"> • 0 kBtu/hr solar • 1.4 stoichiometry 	100	No	Test stopped due to flame outage – test flagged for repeat for SVOC sampling, VOC sample deemed valid (40 minute sample)
5 (repeat of Test 4)	06/23/97	<ul style="list-style-type: none"> • 0 kBtu/hr solar • 1.4 stoichiometry 	120	Yes	No problems encountered
NA ^a	06/24/97	<ul style="list-style-type: none"> • 200 kBtu/hr solar • 1.2 stoichiometry 		No	Clouds appeared before parameters met – test postponed
6	06/26/97	<ul style="list-style-type: none"> • 100 kBtu/hr solar • 1.3 stoichiometry 	120	Yes	No problems encountered
7	06/26/97	<ul style="list-style-type: none"> • 100 kBtu/hr solar • 1.3 stoichiometry 	100	Yes	No problems encountered – SVOCs may be 20% higher due to shorter sample time
8	06/27/97	<ul style="list-style-type: none"> • 100 kBtu/hr solar • 1.3 stoichiometry 	110	Yes	No problems encountered
NA ^a	06/27/97	<ul style="list-style-type: none"> • 200 kBtu/hr solar • 1.2 stoichiometry 		No	Clouds appeared before parameters met – test postponed
9 (repeat of Test 1)	06/28/97	<ul style="list-style-type: none"> • 200 kBtu/hr solar • 1.2 stoichiometry 	109	Yes	No problems encountered

Notes:

^a No test number assigned because the test was postponed due to poor weather conditions.

kBtu/hr = thousand British thermal units per hour
 SVOC = semivolatile organic compound
 VOC = volatile organic compound

4 SAMPLING TECHNIQUES AND ANALYTICAL METHODS

4.1 Introduction

Sampling and analysis of the surrogate waste and flue gas were required throughout the demonstration test to evaluate performance of the solar reactor technology against project goals. To ensure applicable data was obtained, a sampling and analysis plan was developed, as part of the project Test Plan, that refined and implemented strategies to effectively produce valid data under the specific conditions of this test. The overall strategy was based on utilizing standard USEPA sampling and analysis methods, modified to ensure effectiveness for the test, to determine the composition of the surrogate waste feed and the presence of VOCs, SVOCs, O₂, CO, CO₂, NO_x, THC, and HCl in the flue gas. The results of this analysis were used to determine whether or not the system achieved DEs of the POHCs meeting the 99.99 percent destruction requirements.

Specific sampling and analysis requirements and methods employed for the demonstration test are presented in the following paragraphs. Tables 4-1, 4-2, and 4-3 summarize the analytes quantified, sampling and analysis methods used, typical sample gas volumes, and flue gas detection limits for VOCs, SVOCs, and PCDDs/PCDFs, respectively. Note that the detection limits are based on standard analysis of samples in the absence of common interferences; actual detection limits were somewhat higher for samples that required dilution prior to analysis, as discussed in Paragraph 4.3.3.1 and Appendix G. Analytical results are discussed in Section 6 and summarized in Appendix A.

4.2 Sampling Locations and Data Requirements

To support the demonstration, samples were collected and analyzed from the surrogate waste and from the flue gas. Specific sampling locations were selected to ensure that the samples obtained were representative. Paragraph 2.3.4 details the sample collection subsystem of the solar detoxification system; a schematic of the process and the surrogate waste feed and flue gas sample locations was previously illustrated in Figure 2-5.

4.2.1 *Surrogate Waste*

Surrogate waste sampling and analysis were required daily to confirm that all eight constituents were present in approximately the correct proportion for each test. Surrogate waste feed samples were collected and composited for each test condition; only one sample was collected on the days when two tests were conducted. Samples were also collected and composited from the waste storage tank before and after most test conditions.

Surrogate waste samples were analyzed for the eight primary constituent POHCs as listed below:

- TCE (a VOC)
- 1,2-DCB (a VOC)
- Benzene (a VOC)

Table 4-1. Target Volatile Organic Compounds

Compound	Sampling Method	Analytical Method	Analytical Principle	Sampling Time (min)	Sample Vol (Nm ³)	Analytical DL (ng) ^a	Flue Gas DL (µg/dscm)
Chloromethane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Vinyl Chloride	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Bromomethane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Chloroethane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,1-Dichloroethene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Methylene Chloride	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Trans-1,2-Dichloroethene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,1-Dichloroethane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Vinyl Acetate	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	150	8
Chloroform	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,1,1-Trichloroethane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Carbon Tetrachloride	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Benzene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,2-Dichloroethane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Trichloroethene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,2-Dichloropropane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Trans-1,3-Dichloropropene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Toluene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
cis-1,3-Dichloropropene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,1,2-Trichloroethane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3

Table 4-1. Target Volatile Organic Compounds (Continued)

Compound	Sampling Method	Analytical Method	Analytical Principle	Sampling Time (min)	Sample Vol (Nm ³)	Analytical DL (ng) ^a	Flue Gas DL (µg/dscm)
Tetrachloroethene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
cis-1,4-Dichloro-2-butene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	8
trans-1,4-Dichloro-2-butene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Chlorobenzene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Ethyl Benzene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
m,p-Xylene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
o-Xylene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Styrene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
Bromoform	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,1,2,2-Tetrachloroethane	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,3-Dichlorobenzene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,4-Dichlorobenzene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3
1,2-Dichlorobenzene	M0031/Cndnsate	EPA SW-846 M8240	GC/MS	40	0.02	60	3

Notes:

^a Sum of detection limits for three sample train fractions: Tenax[®], Anasorb[®], and condensate

DL = detection limit
GC/MS = gas chromatography/mass spectrometry
min = minute
ng = nanogram (10⁻⁹ grams)
Nm³ = cubic meter
µg/dscm = microgram (10⁻⁶ grams) per dry standard cubic meter

Table 4-2. Target Semivolatile Organic Compounds

Compound	Sampling Method	Analytical Method	Analytical Principle	Sampling Time (min)	Sample Vol (Nm ³)	Analytical DL (µg)	Flue Gas DL (µg/dscm)
Phenol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	5.0	2
2-Chlorophenol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	5.0	2
1,3-Dichlorobenzene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
1,4-Dichlorobenzene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
1,2-Dichlorobenzene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Hexachloroethane	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Nitrobenzene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
bis(2-Chloroethoxy) Methane	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
2,4-Dichlorophenol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	5.0	2
1,2,4-Trichlorobenzene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Naphthalene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Hexachlorocyclopentadiene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	10	4
2,4,6-Trichlorophenol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	5.0	2
2,4,5-Trichlorophenol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	5.0	2
2-Chloronaphthalene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
4-Nitrophenol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	5.0	2
2,4 Dinitrotoluene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Hexachlorobenzene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Pentachlorophenol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	10	4
2,3,4,6-Tetrachlorophenol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	5.0	2

Table 4-2. Target Semivolatile Organic Compounds (Continued)

Compound	Sampling Method	Analytical Method	Analytical Principle	Sampling Time (min)	Sample Vol (Nm ³)	Analytical DL (µg)	Flue Gas DL (µg/dscm)
1,2,4,5-Tetrachlorobenzene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Pentachlorobenzene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
o-Cresol	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Anthracene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Fluoranthene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Pyrene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Butylbenzylphthalate	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Chrysene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Benzo(a)anthracene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
bis(2-Ethylhexyl)phthalate	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Benzo(b)fluoranthene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Benzo(k)fluoranthene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Benzo(a)pyrene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Ideno(1,2,3-c,d)pyrene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Dibenz(a,h)anthracene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4
Benzo(g,h,i)perylene	EPA SW-846 M0010	EPA SW-846 M8270	GC/MS	120	2.5	1.0	0.4

Notes:

DL = detection limit
 GC/MS = gas chromatography/mass spectrometry
 min = minute
 ng = nanogram
 Nm³ = cubic meter
 µg = microgram (10⁻⁶ grams)
 µg/dscm = microgram per dry standard cubic meter

Table 4-3. Target PCDD/PCDF

Compound	Sampling Method	Analytical Method	Analytical Principle	Sampling Time (min)	Sample Vol (Nm ³)	Analytical DL (pg)	Flue Gas DL (pg/dscm)
2,3,7,8-TCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	1.7	0.68
Total TCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	4.4	1.76
1,2,3,7,8-PeCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	1.5	0.6
Total PeCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	2.6	1.04
1,2,3,4,7,8-HxCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	1.9	0.76
1,2,3,6,7,8-HxCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	1.9	0.76
1,2,3,7,8,9-HxCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	1.7	0.68
Total HxCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	1.9	0.76
1,2,3,4,6,7,8-HpCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	1.9	0.76
Total HpCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	2.3	0.92
OCDD	EPA 23	EPA 23	HRGC/HRMS	120	2.5	—	—
2,3,7,8-TCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	2.4	0.96
Total TCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	2.4	0.96
1,2,3,7,8-PeCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.65	0.26
2,3,4,7,8-PeCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.63	0.252
Total PeCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.65	0.26
1,2,3,4,7,8-HxCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.80	0.32
1,2,3,6,7,8-HxCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.69	0.276
2,3,4,6,7,8-HxCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.83	0.332
1,2,3,7,8,9-HxCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.95	0.38
Total HxCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.95	0.38
1,2,3,4,6,7,8-HpCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.75	0.3
1,2,3,4,7,8,9-HpCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.97	0.388
Total HpCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	0.97	0.388
OCDF	EPA 23	EPA 23	HRGC/HRMS	120	2.5	—	—

Notes:

DL = detection limit
 HRGC/HRMS = high resolution gas chromatography/high resolution mass spectrometry
 min = minute
 Nm³ = cubic meter
 pg = picogram (10⁻¹² grams)
 pg/dscm = picogram per dry standard cubic meter

- Ethylbenzene (a VOC)
- Toluene (a VOC)
- Xylene (a VOC)
- Carbon Tetrachloride (a VOC)
- PCP (a SVOC).

Analysis for the seven VOC POHCs was performed using a modified USEPA SW-846 Method 8260 employing gas chromatography/mass spectrometry (GC/MS). Analysis for the one SVOC POHC, PCP, was performed using a modified USEPA SW-846 Method 8270 employing GC/MS. Details on these methods are provided in Paragraph 4.3.3.

It should be noted that analysis of the surrogate waste was only performed for quality control confirmation of the waste preparation: sample analysis before and after each test provided assurance that each waste stream component was present, and in the approximately correct proportion, during each test. The surrogate wastes were prepared quantitatively with higher accuracy (approximately ± 1 percent) than the analytical procedure (approximately ± 10 percent) due to the dilution requirement for analysis. Therefore, surrogate waste concentrations used in the calculation of DE were based on surrogate waste preparation calculations.

4.2.2 Flue Gas

Manual sampling and analysis of flue gas was required to identify concentrations of the target VOCs, SVOCs, and PCDDs/PCDFs⁹, including each of the eight POHCs for this test, listed in Tables 4-1, 4-2, and 4-3. In addition, a CEMS was utilized to analyze flue gas for O₂, CO, CO₂, NO_x, THC, and HCl, as described in Table 4-4. This set of information was used to quantify the DE of the original eight POHCs, and to quantify the formation of PICs (VOCs, SVOCs, and PCDDs/PCDFs) and evaluate other performance parameters against the demonstration objectives (Section 6).

Section 2 describes the sampling section of the flue gas duct, as illustrated in Figure 2-6. A total of six sample ports are contained in the flue gas duct so multiple CEMS, VOC, and SVOC (combined with PCDD/PCDF) samples could be collected simultaneously. CEMS measurements of flue gas composition were conducted both upstream and downstream of the venturi scrubber: a hot, wet sample from downstream of the scrubber was routed to the HCl analyzer while a dry sample collected upstream of the scrubber was sent to the remaining analyzers. Manual method sampling for VOCs, SVOCs, and PCDDs/PCDFs was conducted only upstream of the venturi scrubber.

Details on the CEMS system and daily calibration procedures are provided in Appendix H, along with the CEMS quality assurance/quality control (QA/QC) and test data.

⁹ Emissions of SVOC target analytes were characterized for all test conditions, while emissions of PCDDs/PCDFs were characterized during selected test conditions.

Table 4-4. CEMS Analyzer Specifications

Gas Species	CO ₂	CO	NO _x	HCl	O ₂	Total Hydrocarbons
Instrument Manufacturer and Model No.	Servomex	TECO	TECO 10S	Servomex	Servomex	Cal Instruments
Detection Principle	NDIR	NDIR	Chemiluminescence	GFIR	Paramagnetic	Flame Ionization Detector
Range Utilized	20%	500 ppm	250 ppm	400 ppm	20%	100 ppm
Sensitivity (% of Full Scale)	1	0.5	1	1	0.5	0.5
Interferences	Negligible	CO ₂ 10k:1 H ₂ O 8,500:1	None	Negligible	Negligible	O ₂ 2% of Reading

Notes:

GFIR = gas filter infrared
 NDIR = nondispersive infrared
 ppm = parts per million

Sampling and analysis for VOCs was performed using a modified USEPA SW-846 Draft Method 0031 and SW-846 Method 5040/5041/8240, as described in Paragraphs 4.3.1.2b and 4.3.3.2a, respectively. Sampling for SVOCs and PCDDs/PCDFs was performed using a combined modified USEPA SW-846 Method 0010 and USEPA Method 23, described in Paragraph 4.3.1.2c; analysis for these compounds was performed according to SW-846 Method 8240, described in Paragraph 4.3.3.2b.

Isokinetic sampling was not required for VOCs because all volatile organic species of interest are expected to be in vapor phase at a 204°C (400°F) flue gas temperature. Isokinetic sampling is specified for the SVOC sampling per USEPA SW-846 Method 0010 to ensure representative sampling of particulate and condensed species; however, it could not be conducted for flue gas sampling due to the small inside diameter (3 inches) of the flue gas duct. The small duct diameter limited the accuracy of flue gas velocity measurements made with a pitot tube and precluded use of a full-size sampling nozzle. To compensate for non-isokinetic sampling, the flue gas velocity at this sample location was estimated by mass balance calculations for the reactor and humidification systems, along with measurement of the sample temperature and pressure.

4.3 Methods and Supporting Information

The manual sampling and analysis methods utilized in this test program were developed and validated for organic emissions measurements at hazardous and municipal waste incinerators. Waste incinerators possess a combination of pollution control devices to control organic, particulate, and acid gas emissions. The sampling methods utilized in this test program were developed for the relatively low gas temperatures and acid gas concentrations that were anticipated to be encountered downstream of these pollution control devices.

4.3.1 Manual Sample Collection Procedures

4.3.1.1 Surrogate Waste. Surrogate waste was collected using the waste feed sample valve located between the sample pump and the mass flowmeter. Because the feed flow rate is controlled through feedback control from the mass flowmeter, feed samples were only collected before and after each flue gas manual method sampling test run. Two surrogate waste samples were collected for each test condition and composited into a single precondition sample jar.

4.3.1.2 Flue Gas. Flue gas was manually sampled for VOCs, SVOCs, and PCDDs/PCDFs using standard USEPA methods as described in the following paragraphs. Because high acid (HCl) concentrations were anticipated in the system, an attempt to verify the effectiveness of the standard and modified USEPA sampling methods under high HCl conditions was made prior to the demonstration test.

- a. *Sample Method Verification Test for VOCs and SVOCs.* A Sample Method Verification Test Series was conducted prior to the demonstration test to evaluate the impact of high HCl concentrations on a variety of standard and modified USEPA sampling trains and analysis methods.

During this Sampling Method Verification Test Series, an impinger containing a scrubbing (buffer) solution was inserted between a sample probe and a organic collection resin (Tenax[®] or XAD-2). One standard and one modified VOC and SVOC train configuration were tested at the same reactor test condition during this verification test series. Analysis of the sample train solutions indicated the standard USEPA methods provided equal or superior results to the modified methods. Hence, the methods employed during the initial phase of the demonstration test, as described below, did not utilize a scrubbing solution.

During the demonstration test, it was determined that this Sampling Method Verification Test Series did not provide an adequate evaluation of the impact of the high HCl concentrations. High HCl concentrations had a significant impact on the analysis of the VOC and SVOC samples collected during the Solar Detoxification Test Series. Standard USEPA analytical procedures were modified in response to the HCl interferences. The impact of high HCl concentrations and the subsequent modification of analytical procedures are discussed in detail in Paragraph 4.3.3.2.

- b. *VOCs*. Sampling for VOCs was performed using a modified USEPA SW-846 Draft Method 0031, Sampling Method for Volatile Organic Compounds (SMVOC), for later analysis by GC/MS. The method employs a sampling module and a meter box to sample stationary source effluents. The sampling system is diagrammed in Figure 4-1; details on the method are described in the following paragraphs.

Samples were withdrawn from the flue gas stream through a heated, glass-lined probe. In a modification to the standard method, the probe temperature was maintained at 175°C (347°F) to prevent condensation of several high-boiling-point organic compounds including xylene [140°C (284°F)], ethylbenzene [136°C (277°F)], 1,1,2,2-tetrachloroethane [146°C (295°F)], and dichlorobenzenes [175°C (341°F)]. This modification was recommended by the USEPA and successfully employed during previous test programs by EER.

Withdrawn sample gases were passed through a water-cooled condenser to reduce the temperature to below 20°C (68°F). VOCs were then collected on a set of three sorbent resin traps consisting of a front trap containing Tenax®-GC, a middle trap containing Tenax®-GC, and a back trap containing Anasorb®-747. Liquid condensate was collected in an impinger between the second and third sorbent traps. An impinger containing NaOH was inserted upstream of the meter box to remove HCl.

For each test condition, two 20-liter samples were collected over 40 minutes each. The resin modules were changed between the two sampling events. The first sample set for each test was analyzed; the second sample set was archived for later analysis in the event the first sample set was damaged or contaminated. Condensate samples were preserved in 20-milliliter volatile organic analysis (VOA) vials and analyzed for the presence of organics. For sample preservation purposes, all samples were stored in refrigerators and shipped with ice prior to analysis.

Additional details on sample train preparation, assembly, leak checks, sampling, and recoveries, are provided in the Test Plan.

- c. *SVOCs and PCDDs/PCDFs*. Samples for SVOC and PCDD/PCDF measurements were collected using a combined modified USEPA SW-846 Method 0010, "Modified Method 5 Sampling Train" and USEPA Method 23, "Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans from Stationary Sources" sampling train. A schematic of the combined sampling train is shown in Figure 4-2. Details of the sampling procedure are described in the following paragraphs.

Gaseous and particulate pollutants were withdrawn through a heated probe and passed through a heated filter where organic-laden particulates were collected. Gases were passed through a condenser cooled to 20°C (68°F). SVOCs were

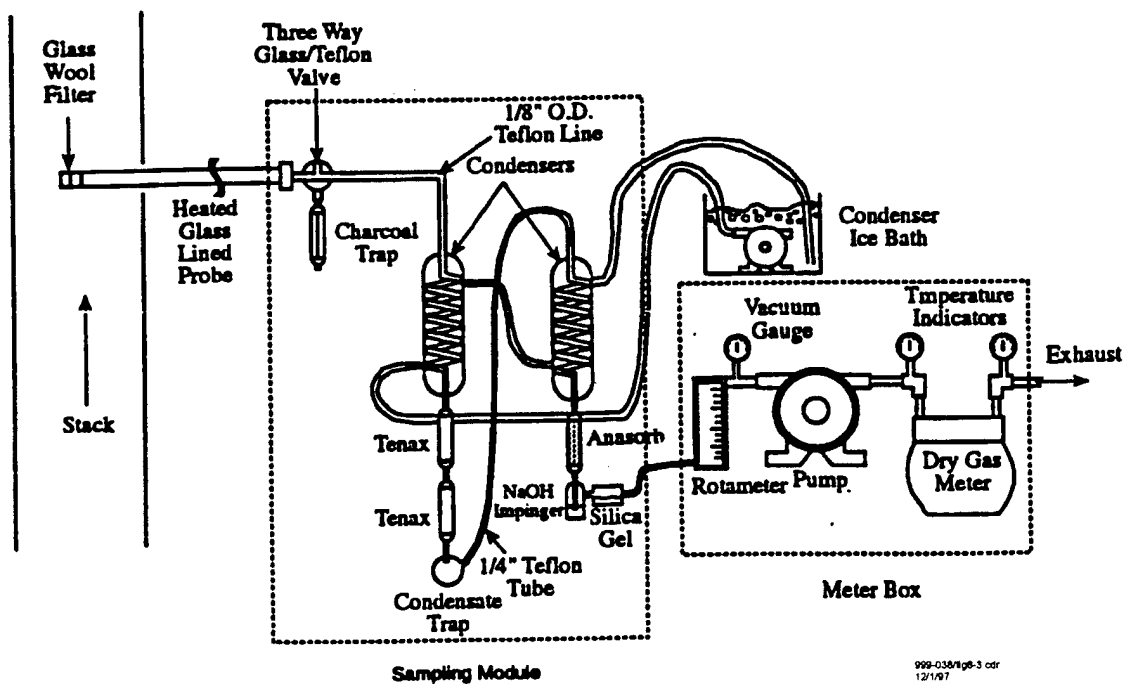


Figure 4-1. Schematic of USEPA SW-846 Draft Method 0031 Sampling Train

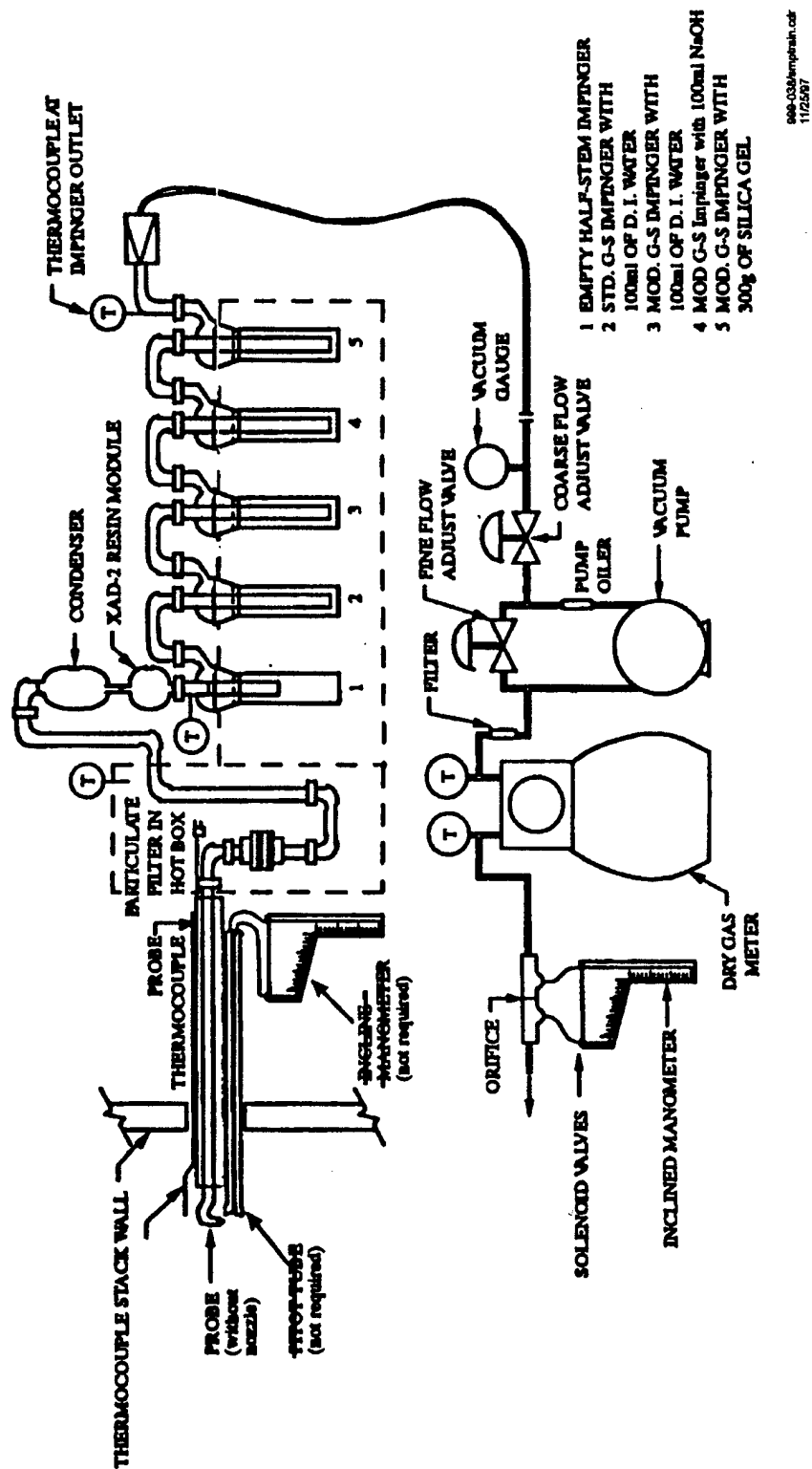


Figure 4-2. Combined USEPA Method 0010/23 Sampling Train Schematic

collected on an Amberlite XAD-2 resin cartridge. Remaining gases then passed through a series of impingers filled with distilled organic-free water.

The USEPA method was modified as shown in Figure 4-2; non-isokinetic sampling was performed at a single point due to the small (3-inch) inside diameter of the flue gas exhaust pipe as described in Paragraph 4.2.2.

After sampling, the filter, XAD-2, and impinger solutions were recovered from the sampling train and extracted on site. Alta Analytical of El Dorado Hills, California, performed sample train extraction for all samples. The Method 0010 (SVOCs) sample recovery protocol specifies solvent rinses with methanol and methylene chloride, while Method 23 (PCDDs/PCDFs) specifies solvent rinses with acetone and toluene. As an alternate reference, California Air Resources Board Method 429 for PAHs specifies acetone, hexane, and methylene chloride rinses. Based on these methods and the requirements of the test, the following rinses were used for sample recovery:

- For tests in which both SVOC and PCDD/PCDF analyses were required, acetone, toluene, and methylene chloride were utilized¹⁰. First the sampling trains were rinsed with acetone, methylene chloride, and toluene; the acetone and methylene chloride rinses were stored separately from the toluene rinse. Then SVOCs and PCDDs/PCDFs were extracted from the filter and sampling train rinses (acetone and methylene chloride rinses only) and XAD-2 resin contents with methylene chloride using a Soxhlet apparatus. The methylene chloride extracts were then combined and divided: one-half was archived, one-quarter was prepared and analyzed for SVOCs, and one-quarter was analyzed for PCDDs/PCDFs.

The filter and sampling train rinses (acetone, methylene chloride, and toluene) were then subjected to an additional extraction with toluene to ensure extraction of the PCDDs/PCDFs. One-quarter of this toluene extract was then combined with the one-quarter of the methylene chloride extract reserved for analysis of PCDDs/PCDFs. Since toluene can interfere with the analysis of some SVOCs, the toluene sampling train rinse was only used in the PCDD/PCDF analysis.

- For tests in which only SVOC sampling and analysis were required, the recovery procedure included only acetone and methylene chloride rinses. SVOCs were then extracted from the filter, both train rinses, and the XAD-2 resin with methylene chloride using a Soxhlet apparatus. The extracts were combined and divided: one-half was archived and the other analyzed for SVOCs.

¹⁰ These solvents were selected based on recommendations by Larry Johnson of USEPA and Bob Mitzel of Alta Analytical, as well as on previous successful sampling experience with this combination train.

Three sets of precleaned glassware were used for SVOC trains to minimize and accurately quantify field blanks. The first field blank was conducted using a train that had not been used for emission/field sampling. The glassware was then rotated so that each set was used for a maximum of three field samples ($9/3=3$). The glassware was cleaned between each field sample to remove residues. The final field blank was collected using glassware that was used for three field samples in order to be representative of all sets of glassware.

For sample preservation purposes, all samples were stored in refrigerators and shipped with ice prior to analysis.

Additional details on sample train preparation, assembly, leak check, and recovery procedures are provided in the Test Plan.

4.3.2 Sample Tracking and Chain of Custody

Acquired data and physical samples required rigorous documentation and safeguarding to maintain data and sample integrity and to ensure against loss of valuable test results. Demonstration testing required the acquisition and compilation of field data, and the physical collection, handling, storage, shipping, and analysis of various types of field samples. All such activities were performed according to strict chain-of-custody procedures, as discussed below.

4.3.2.1 Sample Labeling. The chain-of-custody paperwork was created at the time the sample was collected. As each sample was collected, a sample label was immediately completed and permanently affixed to each sample. Each label had a unique preprinted number that subsequently served as the unique identification number for the sample. Samples were identified by sample location, sample type, test condition, and run number.

4.3.2.2 Sample Tracking and Custody Report. An up-to-date Sample Tracking and Custody Report was maintained throughout the demonstration test. This document included, for each sample, the unique sample identification number, a brief description of the sample, and the destination and subsequent location of the sample. It also specified the analytical procedures to be conducted by the laboratory. Separate field tracking report pages were maintained for the VOC and SVOC trains.

A chain-of-custody form served as a "cradle-to-grave" document that accompanied all samples, tared containers and filters, sample trains, and other specialized sample collection apparatus. The chain-of-custody form satisfied the requirements specified in USEPA/600/4-77/027a2.0.6 and USEPA/600/4-77/077b3.0.3.

Upon receipt of samples, the laboratory observed procedures consistent with previous handling of the samples:

- When samples were received in the laboratory, they were identified by a unique numbering code. This unique number was recorded in a sample log along with date, location of sample, and other related information.

- Samples were preserved as required by procedure.
- Samples requiring immediate or priority attention were identified to begin testing as required.

The field team leader was responsible for proper logging and custody of samples and field data. Run sheets, data sheets, files, and sample tracking forms were completed by each assigned team member. Chain-of-custody forms and laboratory tracking sheets for the demonstration test are reproduced in Appendix E.

4.3.3 Analytical Methods

Analytical procedures for the surrogate waste samples and flue gas samples are described in the following paragraphs.

4.3.3.1 Surrogate Waste. Surrogate waste samples were collected as described in Paragraph 4.3.1.1. The samples were diluted 1,000,000:1 with solvent to prevent detector saturation and resultant damage to the analytical equipment.

- VOCs.** Samples collected from the surrogate waste were analyzed for VOCs using SW-846 Method 8260, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique." Using this method, diluted samples were injected into the gas chromatograph inlet and desorbed onto the gas chromatograph capillary column. The components were separated and detected by low resolution mass spectrometry (LRMS). Calibration standards at a minimum of five times higher concentration were also prepared and analyzed by the same method in reagent water. Quantitation was achieved by comparing the response of the quantitation ion relative to the internal standard using a five-point calibration curve.
- SVOCs.** Surrogate waste samples were analyzed for the SVOC PCP using a modified USEPA SW-846 Method 8270 employing GC/MS. Using this method, a five-point calibration curve was prepared containing the analytes of interest, labeled surrogates, and the internal standards. Diluted samples were spiked with internal standards, introduced into the gas chromatograph using a fused capillary column, and detected by high resolution mass spectrometry (HRMS). Each target compound was quantified based on the recoveries of the compound and the closest eluting internal standard, and the relative response of the internal standard and the target compound. USEPA SW-846 Method 8270 analyses were performed by Air Toxics, Ltd.

4.3.3.2 Flue Gas. Flue gas samples collected for VOCs, SVOCs, and PCDDs/PCDFs were analyzed using modified USEPA methods as described below.

- VOCs.** Collected sorbent tubes were analyzed for VOCs according to the provisions of USEPA SW-846 Method 5040/5041/8240. Air Toxics, Ltd. of

Folsom, California, performed all sample analyses. Surrogate compounds (benzene- d_6 and *cis*-1,2-dichloroethene) were added to one of the Tenax[®] tubes and the Anasorb[®] tube prior to sampling to evaluate the impact of high acid gas levels on compound degradation and recovery.

The pair of Tenax[®] tubes were analyzed separately from the Anasorb[®]-747 tube. After surrogate and internal standards were added to the collected samples, the sorbent tubes were thermally desorbed by heating to 250°C (482°F) and purged with organic-free helium (40 cubic centimeters per minute). The gaseous effluent from the tubes was bubbled through 5 milliliters of prepurged organic-free reagent water for 11 minutes and then trapped in a purge-and-trap unit. The analytical adsorbent trap of this unit contained Tenax[®]-GC, methyl silicone packing, silica gel, and coconut charcoal. The trap was then heated rapidly to 250°C (482°F) and the gas flow from the analytical trap directed to the head of a fused silica capillary column (DB-624 column or equivalent). The column was maintained initially at subambient temperatures to refocus the organic species and then temperature-programmed to resolve the mixture. A low-resolution mass spectrometer operated in the full scanning mode was used for peak identification and quantification.

Each VOC was quantified based on the recoveries of the target VOC and the closest eluting internal standard, and the relative response of the internal standard and target VOC. Results are reported in Section 6.

Analytical problems were encountered for one early Anasorb[®] sample (2401B) due to high CO₂ concentrations. The high CO₂ concentrations saturated the detector and shut down the analytical instrument. For the following two Anasorb[®] samples (4209B and 4207B), the GC/MS was modified to start scanning at 2 minutes, instead of 0 minutes, to avoid the CO₂ elution. This modification resulted in the loss of analytical results for low molecular-weight VOCs including chloromethane.

Analytical results were also unavailable from several samples because the analytical instrument was damaged or shut down due to high acid concentrations in the Tenax[®] and Anasorb[®] tubes. The VOC analytical procedures were subsequently modified to mitigate the damaging impacts and interferences of the high HCl concentrations using a bag methodology.

The bag dilution methodology involved the thermal desorption of the sorbent tube into a Tedlar bag. After the sample was desorbed, the gas phase sample was screened using a gas chromatograph equipped with a flame ionization detector (GC/FID). From this screen, the analyst determined the appropriate amount of sample to inject into the GC/MS system. After determination was made, the calculated volume of sample was injected onto a clean sorbent tube and the tube subsequently analyzed using standard procedures. Dilution ratios for this test series varied from 0 to 3,200. It should be noted that it was possible to inject the

entire volume of the Tedlar bag onto the clean volatile organic sampling train (VOST) tube without loss when dilution was not required.

This dilution methodology was previously utilized and validated by Air Toxics, Ltd. During preliminary validation of this methodology, the efficiency of the transfer was evaluated by injection of a known amount of benzene-d₆ onto the sorbent tube prior to desorption. Recoveries of 95 to 97 percent were seen during these preliminary validation tests. In the current test series benzene-d₆ was not injected onto the sorbent tube prior to desorption because it had already been injected onto the tubes prior to sample collection. The data quality for the current test series was impacted by the high dilution ratios and the sample-to-sample variation in dilution ratios. The impact of utilization of the dilution methodology is discussed in more detail in Appendix G1.

USEPA SW-846 Method 8240, based on a purge and trap detected by GC/MS, was used for analysis of the condensate samples. This method can be used to quantify most VOCs that have boiling points below 200°C (392°F). For the condensate analysis, 20-milliliter sample vials were used, and a larger sparger was used for analysis to reduce the method detection limit to 40 ng.

- b. *SVOCs and PCDDs/PCDFs.* SVOCs were determined by analysis of an aliquot of the sample train extract following the high resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) procedures of USEPA SW-846 Method 8270. Dilution of the extracted SVOC samples was required to negate the impact and interferences of the high HCl concentrations. The sample dilution ratios varied from 10:1 to 25:1. PCDDs/PCDFs were quantified by analysis of the sample aliquot following the capillary column high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) procedures of USEPA Method 23. Each target compound was quantified based on the recoveries of the compound and the closest eluting internal standard, and the relative response of the internal standard and the target compound.

USEPA SW-846 Method 8270 analysis was performed by Air Toxics Ltd. and Method 23 analysis was performed by Alta Analytical.

4.4 Calibration Procedures

All equipment used in the demonstration test was maintained and calibrated using standard procedures and USEPA, American Society for Testing and Materials (ASTM), and/or National Institute of Standards and Technology (NIST) traceable reference equipment where applicable. Calibrations were performed routinely prior to fielding the equipment; the equipment was checked in the field to assure that handling and use had not affected the calibrations. Following the test, the equipment calibration was checked to verify calibration throughout the test.

Calibration was performed as indicated in the Test Plan; procedures for specific analytical equipment are provided in the following paragraphs.

4.4.1 *Thermometers and Thermocouples*

Bimetallic stem thermometers and thermocouple temperature sensors were calibrated using the procedure outlined in Section 3.4.2 of USEPA Document 600/4-77-027B. Each temperature sensor was calibrated at a minimum of three points over the anticipated range of use against a NIST-traceable thermometer. All sensors were calibrated prior to field sampling.

4.4.2 *Dry Gas Meters*

Dry gas meters used in USEPA SW-846 sampling trains (Paragraphs 4.3.1.2b and 4.3.1.2c) were calibrated just prior to fielding of the equipment. A post-test calibration check was performed upon return to the laboratory. Pre- and post-use calibrations were required to agree within 5 percent.

Dry gas meters were calibrated using a positive pressure leak-check as described in Section 3.3.2 of USEPA Document 600/4-77-27b. The system was placed under approximately 10 inches of water pressure and a gauge oil manometer used to measure any pressure decreased over one minute. If leaks were detected, they were fixed prior to calibration.

After leak-checking, the pump was allowed to warm up for 15 minutes. The valve was then adjusted to the desired flow rate. For pre-test calibrations, data were collected at orifice manometer settings of 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 inches of water. Gas volumes of 5 cubic feet were used for the two lower orifice settings, and volumes of 10 cubic feet for higher settings. The individual gas meter correction factors were calculated for each orifice setting and averaged. Each of the individual correction factors was required to fall within 2 percent of the average correction factor.

For post-test calibration, the meter was calibrated three times at the average orifice setting and the highest vacuum used during the demonstration test.

4.4.3 *Analytical Balance*

Analytical balances were calibrated prior to use over the expected range of use with standard weights (NIST Class S). Measured values were required to agree within ± 0.1 milligram.

4.4.4 *CEMS*

CEMS calibration was performed daily; the procedures are detailed in Appendix H.

5 QUALITY

5.1 Introduction

During the demonstration test, a range of data measurements were conducted, including cooling water flow rate and inlet and outlet water temperature, reactor exit gas temperature, flue gas composition (CO₂, O₂, CO, NO_x, and THC), flue gas organics (VOCs and SVOCs), stack gas HCl, waste feed rates, and excess air flow. To ensure the data was of sufficient quality to evaluate the performance of the solar reactor, QA and QC were applied throughout the test. The following paragraphs summarize the application of QA/QC during the demonstration test and the quality of the data produced.

5.2 Quality Assurance/Quality Control Requirements

QA encompasses the organization and written program within which QC activities are performed. QC activities accompany testing, engineering, and other procedures to provide control of data quality and quantify the quality of data resulting from those procedures. A QA/QC program is critical to successful testing, because it assures higher quality, more reliable test results than may be obtained otherwise, provides a means to determine the level of data quality obtained, and can assure that test results will be comparable to similar data and tests.

The objective of the QA effort for this project was to assess and document the quality of measurement data. Prior to the test, a written Quality Assurance Project Plan (QAPjP) was developed as part of the Test Plan. The QAPjP was developed in accordance with USEPA's requirements for a Category III project¹¹, as defined in "Preparation Aids for the Development of RREL Quality Assurance Project Plans, USEPA, Risk Reduction Engineering Laboratory" (USEPA Risk Reduction Engineering Laboratory, Cincinnati, Ohio, 1989). The resulting QAPjP included a detailed description of the following subjects:

- QA approach
- QA/QC organization
- QA objectives
- Data reduction, validation, and reporting requirements
- QC procedures requirements
- Technical systems and performance evaluation audits
- Calculation of data quality indicators
- Corrective actions.

QC was implemented throughout the test, as described in the QAPjP. QC samples, such as reagent blanks, field blanks, trip blanks, lab blanks, laboratory control samples and spikes, method blanks, and method spikes were employed as projected. Pre- and post-test QA/QC was employed to ensure and confirm equipment operated correctly and samples were handled and analyzed correctly. Performance audits were also conducted.

¹¹ Category III is applicable to projects producing results used for engineering, technology development, feasibility studies, or preliminary assessments.

Data was validated internally by QC personnel. All measurement data was validated based on process conditions during sampling or testing, acceptable sample collecting/testing procedures, consistency with expected results, adherence to prescribed QC procedures, and specific acceptance criteria. The QA Coordinator, reporting directly to EER Corporate officials, was primarily responsible for performing Test Plan review, on-site performance and system audits, analytical system and performance audits, and reporting of all QA/QC activities and data.

The QAPjP established specific DQOs for precision, accuracy, representativeness, completeness, and comparability, as described in Paragraph 5.3. Throughout the demonstration test, data quality was assessed against these objectives to determine if the measurement data, such as temperature and pH measurements, were of sufficient quality that an appropriate assessment of the technology could be performed.

5.3 Data Quality Objectives

DQOs are qualitative and quantitative statements that specify the quality of data required from a particular activity. The DQOs are the standards against which the data generated can be evaluated. The USEPA provides the basis for developing the DQOs for an individual project.

DQOs must address five data characteristics:

- Precision
- Accuracy
- Representativeness
- Completeness
- Comparability.

A sixth data characteristic, level of detection, should also be addressed when possible.

Precision, accuracy, and completeness DQOs for sampling and analytical methods are provided in Table 5-1. Additional details on selection and calculation of these DQOs are provided in the Test Plan. The following paragraphs briefly describe these data characteristics; QA/QC results are presented with data in the various appendices.

5.3.1 Precision

Precision is a measure of agreement, or lack of variability, among different analyses performed using the same test method. It is estimated by determining the standard deviation between replicate samples. To evaluate precision during the demonstration test, each test method contained provisions for duplicate analytical samples such as method spikes (referred to as laboratory control samples). Precision was then assessed by analyzing the duplicate samples, calculating the relative standard deviation (RSD)¹², and comparing the RSD to the DQO.

The demonstration test involved a screening study of process variables utilizing standard statistical analysis of a TLFD. To appropriately interpret the results, measurement variability

¹² RSDs of less than 25 percent are typically sufficient for most data.

Table 5-1. Data Quality Objectives

Measurement	Sampling Method	Analytical Method	Analytical Precision (%)	Overall Precision (%)	Accuracy (%)	Completeness (%)
VOCs	SW-846 Draft Method 0031	SW-846 Method 5040/5041/8240	±30	±30	±35	100 ^a
SVOCs	SW-846 Method 0010	SW-846 Method 8720	±50	±87	±50	100 ^a
PCDDs/PCDFs	Method 23	Method 23	±50	±87	±50	100 ^a

Notes:

^a Incomplete measurements were required to be repeated

PCDDs/PCDFs = dioxins/furans

SVOCs = semivolatile organic compounds

VOCs = volatile organic compounds

should be minimal and precision should be maximized, allowing process variables that have significant impact, such as stoichiometry and insolation, to be clearly identified.

To minimize measurement variability, an attempt was made to maximize sampling precision, sample recovery precision, and analytical precision. Triplicate runs on one set of test conditions were performed to provide an indication of process repeatability that could be used in point-by-point analysis of the results. The precision of results from the three replicate tests indicates the overall variability of the process and measurements including process, sampling, recovery, and analytical variability.

The statistical analysis results, which implicitly account for overall precision, are presented in Paragraph 6.4.1 and Appendix F. Analytical precision was assessed through evaluation of the relative percent difference (RPD) for laboratory control samples or the RSD for surrogate compound recoveries.

5.3.2 Accuracy

Accuracy is the agreement of a measurement (or average of measurements) with an accepted reference or true value. For example, in laboratory analysis, accuracy indicates the amount of analyte detected as compared to the amount actually present. QA/QC activities evaluating accuracy provide information to confirm that the results are unbiased and represent true values.

Each test method used for this demonstration test contains or refers to procedures for calibration of sampling and analytical equipment. Spiked samples, such as pretest resin spikes, field spikes, and laboratory method spikes, are used to calculate whether acceptable recovery has been

achieved. Blank sample trains and laboratory method blanks are also analyzed to determine if contamination may have affected results.

Achievement of accuracy DQOs during the demonstration is presented in Paragraph 6.4.2.

5.3.3 Representativeness

Representativeness expresses degree to which a sample, or a group of samples, reflects that characteristics of the media at the sampling point. It is a qualitative parameter impacted by the design of the sampling program. The representativeness criterion is best satisfied by proper selection of the sampling locations, and by ensuring a sufficient number of samples are collected.

In the demonstration test, procedures were designed so that samples taken were representative of the flue gas characteristics. Test samples were taken from test locations in accordance with the standard USEPA methods with the exception of SVOC samples (Section 4). To maximize representativeness, samples were taken during normal operations of the process, and testing was suspended if the process appeared to deviate from normal operation.

5.3.4 Completeness

Completeness is a measure of the amount of valid data collected compared to the amount that was expected to be obtained under correct operating conditions. Completeness is calculated by dividing the number of validated data points by the number of samples collected for analysis. The DQO development process for completeness must consider that not all samples will remain intact through the entire measurement process: sample containers may be broken, instruments may go outside control limits, data may be lost, sample identifications may become illegible, or other conditions may occur that limit the data available from a specific sample.

The DQO for completeness was set to 100 percent for the demonstration test. A complete test was defined as including the collection and analysis of all emissions and QA/QC samples specified in the test plan. Factors anticipated to impact the completeness of the demonstration test data included poor weather conditions, limited daylight hours, upset in facility operation, accidental loss of sample, or invalidation of sample results for other reasons.

The test matrix, as defined in the Test Plan and described in Paragraph 3.3, was modified midway through the test due to poor weather conditions and time constraints. All of the test conditions and samples specified in the revised test matrix were completed.

5.3.5 Comparability

Comparability is a measure of the confidence with which one data set can be compared with another. Comparability is achieved by using consistent methods and standards that are traceable to a reliable source, such as the use of USEPA standard analytical methods (Paragraph 4.3.3).

One of the primary objectives of the test program was to "achieve low levels of PICs and show that the compounds of greatest concern, based on toxicity, are at or below levels typically

emitted from hazardous waste incinerators.” For the purpose of this screening study, the PIC emissions for a selected set of operating conditions and a select number of compounds were compared with emissions from hazardous waste incinerators. This comparison is only preliminary, since triplicate measurements indicating process reproducibility were not performed for each condition. The results of this comparison are included in Paragraph 6.3.2 and shown in Figures 6-4, 6-5, and 6-6.

The unique sampling location and operation of the solar reactor make direct comparison to conventional hazardous waste incinerators somewhat difficult. As discussed in Paragraph 2.3.4, manual method sampling for conventional hazardous waste incinerator trial burns is conducted downstream of the units’ pollution abatement system(s), whereas sampling of the solar reactor occurred upstream of the unit’s exhaust gas subsystem. Because VOCs and SVOCs can potentially be removed in the exhaust gas subsystem, a direct comparison of analytical results is not appropriate.

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6 TECHNOLOGY DEMONSTRATION RESULTS AND EVALUATION

6.1 Introduction

This section summarizes the demonstration test results and evaluates system and individual subsystem performance against the overall and specific demonstration objectives summarized in Section 1. Data quality achieved is also described. Based on these results, suggestions are made for future modifications that may enhance system operation and efficiency. The performance of the solar detoxification system is also compared to other technologies for destruction of organic wastes, and the economic factors of the technology are analyzed.

6.2 Subsystems Performance

The first goal of the demonstration test, as summarized in Section 1, was to demonstrate the operation of a dish-mounted solar detoxification system and identify operating envelopes for the process. The solar detoxification system was operated successfully during the demonstration test. Operating envelopes identified for each subsystem during the test are described in the following paragraphs.

6.2.1 Solar Concentrator Subsystem

The solar energy concentrator, sun tracking, and energy transmission into the reactor performed as designed. The solar concentrator and reactor were operable while tracking the sun from horizon to horizon.

During the operation of the reactor, solar insolation was measured by a dish-mounted NIP. The recorded solar flux data for on-sun test days are presented in Table F-3, Appendix F-5. These data were corrected by a calibrated portable NIP. The calibration data are also included in Appendix F-5.

The average solar flux during testing was 910 watts per square meter (W/m^2), with a standard deviation of 41 W/m^2 . Maximum solar flux is approximately 1,000 W/m^2 . Therefore, the reactor operated at slightly less than the maximum insolation levels. Tests 1, 3, and 9 (Test 9 was the repeat of Test 1) required 200 kBtu/hr solar input and required that all 16 of the concentrator's facets be in service. During the triplicate center point tests (Tests 6, 7, and 8) requiring 100 kBtu/hr solar input, the number of facets in service were reduced from 16 to 8, which halved the solar input.

The cloudy weather in Golden, Colorado during the month of June effected the solar insolation, with occasional clouds of varying density passing between the sun and the dish during test periods. In some instances, sampling was stopped for several minutes while the cloud(s) moved away and the reactor came back to temperature. Because the reactor operated between 0 and 200 kBtu/hr solar input extremes, the resulting small variation (less than 20 kBtu/hr) in insolation during on-sun tests was assumed to be relatively insignificant in changing the reactor's performance. In other cases, the testing was rescheduled for another day.

6.2.2 Surrogate Waste Storage Subsystem

The SWSS performed as designed with no operational problems impacting data quality.

The results of the surrogate waste daily composite QC analyses are presented in Table F-2 of Appendix F-4. The analyses did not identify any significant problems with the surrogate waste composition, although the measured TCE, ethylbenzene, and PCP concentrations were consistently different than the calculated composition from known quantities added. This difference is most likely due to analytical uncertainty caused by the 1,000,000:1 sample dilution prior to analysis. The VOC analyses conducted by SW-846 Method 8260 for TCE and ethylbenzene can have recoveries between 80 and 120 percent; the SVOC analyses conducted by SW-846 Method 8270 for PCP can have recoveries between 20 and 100 percent. Based on the consistent surrogate waste preparation procedures and consistent laboratory results, no deviations for the target surrogate waste composition are evident.

6.2.3 Solar Reactor Subsystem

6.2.3.1 Parametric Test Results. The final test design and operating parameters defined in Section 3 reflect the system capabilities observed during the system checkout. These parameters were controlled as specified during the tests. Temperature and heat transfer effects discussed in this paragraph reflect the thermal performance of the reactor. Subsequent paragraphs address the effects on surrogate waste detoxification and emissions performance under these same reactor conditions.

Statistical analyses were performed for the reactor operating temperatures and heat balance results. The statistical analyses included an evaluation of the primary effects, analysis of variance, evaluation of residuals, and interpretation of results. The statistical analyses for the reactor operation included analysis of reactor exit gas temperature, reactor exit gas heat content, cooling water heat extraction, and the miscellaneous reactor heat losses through the refractory and quartz window. The statistical analysis software printouts are provided in Appendix F-1. The operating data used in the following analyses are summarized in Table 6-1; conclusions formed from this data are provided in section 7 of this report.

6.2.3.2 Exit Gas Temperature. The reactor exit gas temperatures ranged from 480°C (900°F) to 650°C (1200°F) over the operating conditions tested. Thermodynamic modeling predicted that exit gas temperatures for 1.2 stoichiometry would be 700°C (1,300°F), which is substantially higher than the actual temperatures. A plot of the reactor gas time-temperature history is provided in Figure 6-1 for the 1.2 stoichiometry during on-sun and off-sun operations. Heat losses were much greater than expected. While these heat losses were not quantified, they had the effect of forcing reactor operations at low excess air levels where a stable flame could be sustained.

Statistical analysis showed that solar insolation had a significant effect (probability greater than 99.99 percent) on exit gas temperature while the effect of stoichiometry on exit gas temperature

Table 6-1. Summary of the Reactor Operating Data

Test No.	Test ID	Date	Test Start Time	Test Stop Time	Waste Heat Input (Btu/hr)	LPG Pilot Heat (Btu/hr)	Solar Heat Input (Btu/hr)	Reactor Stoich.	Gas Flow Rate (lb/hr)	Exit Gas Temp. "A" (°F)	Exit Gas Temp. "B" (°F)	Exit Gas Temp. "A and B" (°F)	Exit Gas Heat Content (Btu/hr)
1	062097001	6/20/97	11:15 AM	12:02 PM	170,000	30,000	200,000	1.20	176	1,144	1,178	1,161	54,033
1	062097001	6/20/97	12:02 PM	12:50 PM	170,000	30,000	200,000	1.20	176	1,231	1,205	1,218	56,882
1	062097001	6/20/97	12:50 PM	12:58 PM	170,000	30,000	200,000	1.20	176	1,202	1,210	1,194	55,682
1	062097001	6/20/97	12:58 PM	1:30 AM	170,000	30,000	200,000	1.20	176	1,154	1,135	1,144	53,183
2	062097002	6/20/97	8:24 AM	6:35 PM	170,000	30,000	0	1.20	176	877	957	917	41,837
3	062197001	6/21/97	12:05 PM	2:30 PM	170,000	30,000	200,000	1.40	203	1,161	1,159	1,159	62,207
4	062197002	6/21/97	3:45 PM	5:25 PM	170,000	30,000	0	1.40	203	958	961	960	50,734
5	062397002	6/23/97	6:00 AM	6:00 AM	170,000	30,000	0	1.40	203	944	996	970	51,310
6	062697001	6/26/97	9:45 AM	11:45 AM	170,000	30,000	100,000	1.32	190	1,116	1,085	1,100	55,039
7	062697002	6/26/97	12:20 PM	2:03 PM	170,000	30,000	100,000	1.33	190	1,108	1,068	1,088	54,392
8	062797001	6/27/97	8:55 AM	10:45 AM	170,000	30,000	100,000	1.31	190	1,118	1,075	1,097	54,877
9	062897001	6/28/97	8:20 AM	10:25 AM	170,000	30,000	200,000	1.20	176	1,163	1,216	1,190	55,482

Table 6-1. Summary of the Reactor Operating Data (Continued)

Test No.	Test ID	Date	Test Start Time	Cooling Water Flow Rate (gpm)	Water Inlet Temp. (°F)	Water Outlet Temp. (°F)	Water Delta Temp. (°F)	Cooling Water Heat Extraction (Btu/hr)	Total Heat Input (Btu/hr)	Total Heat Extracted and Exiting (Btu/hr)	Other Heat Loss (Btu/hr)
1	062097001	6/20/97	11:15 AM	18.3	109.0	130.0	20.7	188,647	400,000	242,680	157,320
1	062097001	6/20/97	12:02 PM	21.2	115.8	134.6	18.7	197,427	400,000	254,309	145,691
1	062097001	6/20/97	12:50 PM	25.3	118.9	135.0	16.0	201,590	400,000	257,273	142,727
1	062097001	6/20/97	12:58 PM	29.9	112.0	127.5	15.4	229,309	400,000	282,492	117,508
2	062097002	6/20/97	8:24 AM	30.9	103.0	110.0	7.0	107,717	200,000	149,554	50,446
3	062197001	6/21/97	12:05 PM	30.2	96.7	109.0	12.5	187,995	400,000	250,202	149,798
4	062197002	6/21/97	3:45 PM	30.2	91.2	96.8	5.6	84,222	200,000	134,956	65,044
5	062397002	6/23/97	6:00 AM	30.3	90.2	96.4	6.2	93,554	200,000	144,865	55,135
6	062697001	6/26/97	9:45 AM	30.2	88.1	98.7	10.6	160,021	300,000	215,061	84,939
7	062697002	6/26/97	12:20 PM	30.2	95.1	105.4	10.3	155,209	300,000	209,600	90,400
8	062797001	6/27/97	8:55 AM	30.2	95.8	106.0	10.3	155,359	300,000	210,236	89,764
9	062897001	6/28/97	8:20 AM	30.0	98.2	111.6	13.4	200,196	400,000	255,678	144,322

Notes:

Btu/hr = British thermal units per hour
 gpm = gallons per minute
 lb/hr = pounds per hour
 LPG = liquefied petroleum gas
 stoich. = stoichiometry

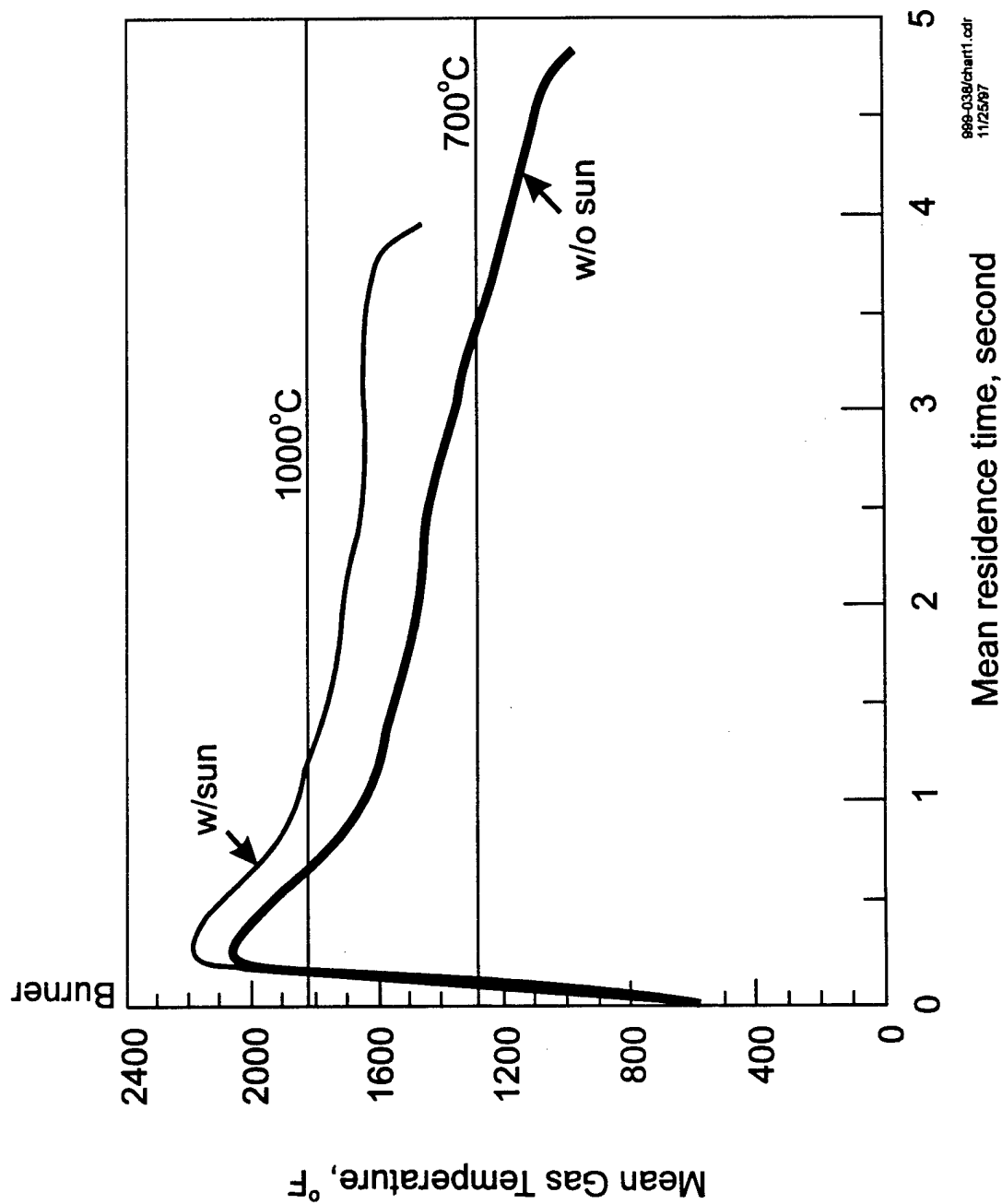


Figure 6-1. Mean Time-Temperature History of Reactor Gases at 1.2 Stoichiometry With 200 kBtu/Hr Solar Input and Without Solar Input

was not significant. The statistical analyses indicate that solar insolation has a linear impact on exit gas temperature described by the equation:

$$\text{Exit Gas Temperature (}^{\circ}\text{F)} = 949 + 1.12 * \text{Insolation (kBtu/hr)} \quad (\text{Eq. 6-1})$$

The reduced stoichiometries of 1.2 to 1.4 used during testing caused hotter flame zone temperatures and increased the gas residence time. Both effects increase heat loss. Thus, hotter flame zone temperatures, which might be expected to increase exit gas temperature, are offset by increased heat loss.

The model also shows that the reactor gases achieve almost 4 seconds of residence time in the temperature range between 480°C (900°F) and 650°C (1,200°F). This longer residence time is a consequence of reducing the combustion air feed rate. The original design conditions employing higher air feed rates with stoichiometries as high as 2.65 would provide just over 1 second of residence time in this temperature window. However, as noted previously, the reactor could not be operated at the design air feed rate due to the flame stability issues.

6.2.3.3 Exit Gas Heat Content. While the exit gas temperature was predominately affected by solar insolation, based on the statistical analysis (presented in Appendix F-1) the exit gas heat content was impacted by both stoichiometry and insolation. Increasing the stoichiometry does not effect exit gas temperature, but does increase the mass flow through the reactor, causing a proportional increase in total heat content. At low stoichiometry (1.2), the solar insolation has a more pronounced effect on exit gas heat. The impact of stoichiometry and solar insolation on the reactor's exit gas heat is shown in Figure 6-2.

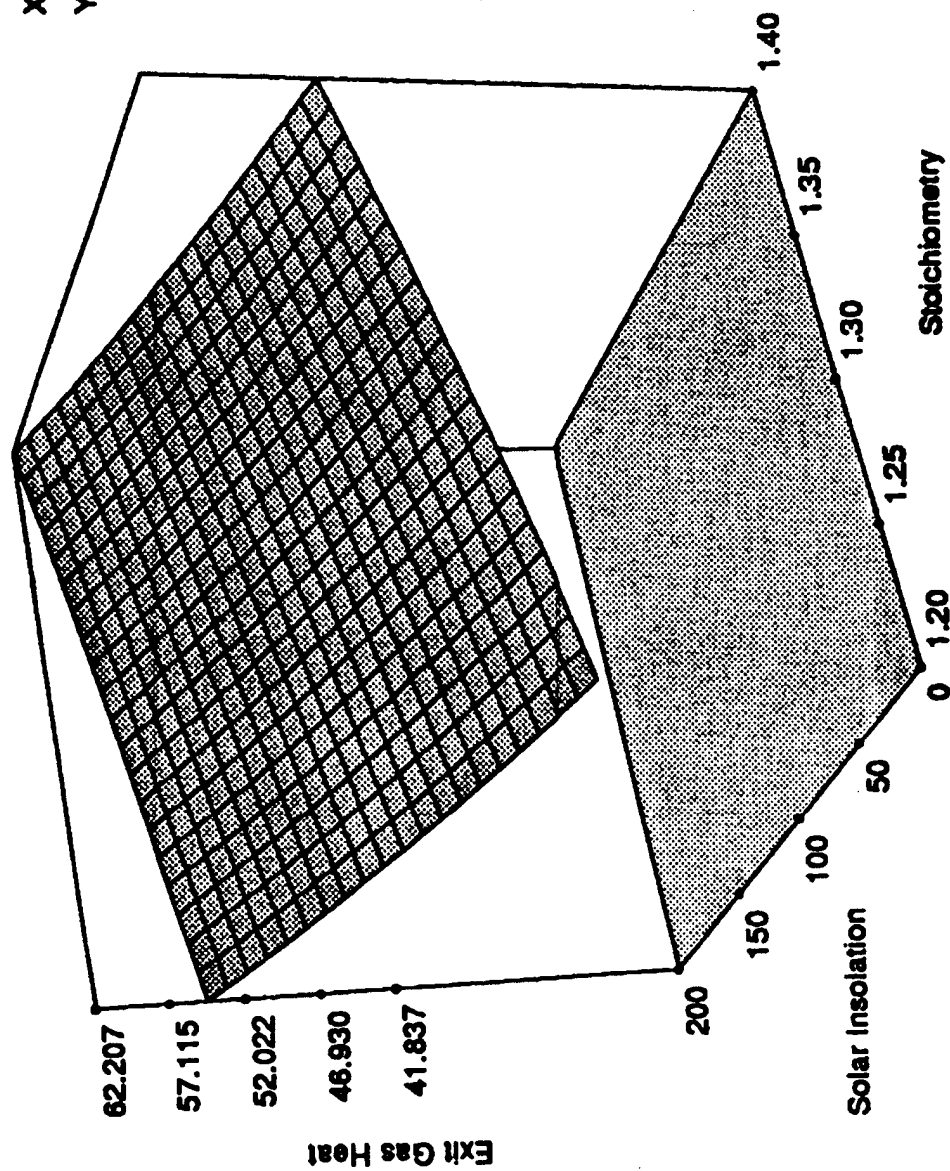
6.2.3.4 Cooling Water Heat Extraction. Approximately 45 percent of the total heat input from both chemical and solar sources was extracted by the reactor's water-cooled entrance region. Statistical analysis indicates that water heat extraction was not affected by changes in stoichiometry, but that it was affected by solar insolation. The analysis indicates with a high degree of confidence (greater than 99.99 percent) that supplying 200 kBtu/hr of solar insolation approximately doubled the heat extracted. This is consistent with design expectations that solar energy initially heats the walls of the reactor rather than being absorbed directly by the gases CO₂, N₂, and O₂, which have primary absorptions in the infrared (IR) rather than the visible range. The influence of solar insolation on cooling water heat extraction is given by the following equation:

$$\text{Water Heat Extraction (kBtu/hr)} = 95.2 + 0.49 * \text{Insolation (kBtu/hr)} \quad (\text{Eq. 6-2})$$

6.2.3.5 Reactor Heat Loss. All of the energy inputs to the reactor are matched by energy outputs represented by exit gas heat content, water heat extraction, and reactor heat losses. Reactor heat losses include conduction through the refractory-lined wall sections and the quartz window. The statistical analysis indicates that these miscellaneous heat losses are also primarily affected by solar insolation. The heat loss behavior through the refractory and quartz window is described by the equation:

$$\text{Misc. Heat Loss (kBtu/hr)} = 56.9 + 0.47 * \text{Insolation (kBtu/hr)} \quad (\text{Eq. 6-3})$$

Actual Factors:
 X = Stoichiometry
 Y = Solar Insolation



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Figure 6-2. Statistically Generated Response of Reactor Exit Gas Heat Content Versus Solar Input and Stoichiometry

6.3 Overall System Performance Against Established Goals

The demonstration test was designed to characterize the solar detoxification system's performance by collecting flue gas samples upstream of the exhaust gas subsystem and analyzing them to determine the DE of POHCs, the formation of PICs, and the production of criteria pollutants and HCl. The following paragraphs present the analytical results for these tests, and compare them to the respective test objectives.

6.3.1 Principal Organic Hazardous Constituents

An important demonstration test objective was to achieve a DE for POHCs that met or exceeded the 99.99 percent destruction and removal efficiency (DRE)¹³ required under RCRA for facilities treating hazardous wastes.

To establish the DE, it is necessary to know the inlet and exit flow rate of the surrogate waste compounds. The inlet feed characterized in Table 3-5 includes chlorinated and aromatic hydrocarbons representative of compounds anticipated to be recovered in soil remediation activities. The surrogate waste feed rate for the tests was 19.4 pounds per hour (lb/hr).

The calculated DE performance is presented in Table 6-2 and is based on the surrogate waste feed rate and the flue gas emissions data which are summarized in Appendix A and presented in Appendix B. DE has been calculated using two methods to illustrate the effect of detection limits on DE variability: (1) assuming concentrations of non-detected compound concentrations are present at the full analytical detection limit; and (2) assuming non-detected compound concentrations are zero. This latter condition is not expected to be adopted for permit activities, but does indicate the operation limits for any future tests if lower detection limits are available. Table 6-2 presents each calculated DE result for Tests 1 through 9, excluding Test 4, which had a flame outage prior to completion of the test run.

The overall DE for total POHCs ranged from 99.98806 to 99.99974 percent using these two calculation methods. For example, for the 200 kBtu/hr solar insolation tests at 1.2 (Test 9) and 1.4 stoichiometry (Test 3), respectively, the calculated DE of total POHCs were 99.99685 and 99.99951 percent, respectively, when concentrations of non-detected compounds are set to equal the analytical detection limit. By setting concentrations of non-detected compounds to zero, the DE for total POHCs increases to 99.99959 and 99.99966 percent, respectively.

Figure 6-3 presents the waste DEs for total VOC and SVOC POHCs. DE for total VOC POHCs ranged from 99.98757 to 99.99998 percent, setting concentrations of non-detects to the full detection limit. The worst DE percent occurred at one of the center point conditions (Test 6). This VOC DE increased to 99.99904 percent when concentrations of the non-detects were set equal to zero. DE for SVOC POHCs ranged from 99.99922 to 99.99979 percent with

¹³ DRE is used to measure the effectiveness of RCRA permitted waste treatment processes. Results are typically presented as DRE when the overall performance includes thermal destruction of toxic organics in the reactor and removal of trace residuals by an exhaust gas subsystem. Because the solar detoxification system flue gas emissions were measured upstream of the exhaust gas subsystem, the performance is characterized as DE, rather than DRE.

Table 6-2. Summary of Calculated Waste Destruction Efficiencies for Demonstration Tests

Test Number	1	2	3	4	5	6	7	8
Solar Input, kBTU/hr	200	0	200	0	0	100	100	100
Stoichiometry	1.2	1.2	1.4	1.4	1.4	1.3	1.3	1.3
Total POHC Feed Rate								
Total POHC Emission Rate (nd = full detection limit (DL))	7416311.35	7416311.35	7416311.35	7416311.35	7416311.35	7416311.35	7416311.35	7416311.35
DE of Total POHC (nd = full DL)	10.9	233.2661491	36.68407779	39.73183795	885.534518	365.3780037	406.1135558	406.1135558
Total POHC Emission Rate (nd = 0)	99.99985	99.99685	99.99974	99.99951	99.99946	99.98806	99.99507	99.999452
DE of Total POHC (nd = 0)	100.00000	30.24751303	14.22141475	25.31923517	28.39443189	67.79836221	70.53326089	30.57389638
VOC POHC Feed Rate								
VOC POHC Emission Rate (nd = full detection limit (DL))	7045495.78	7045495.78	7045495.78	7045495.78	7045495.78	7045495.78	7045495.78	7045495.78
DE of VOC POHC (nd = full DL)	NA	223.3661491	14.44657405	25.58407779	28.43183795	875.434518	349.9780037	394.5135558
VOC POHC Emission Rate (nd = 0)	99.99985	99.99683	99.99979	99.99964	99.99960	99.98757	99.99503	99.99440
DE of VOC POHC (nd = 0)	100.00000	30.24751303	14.22141475	25.31923517	28.39443189	67.79836221	70.53326089	30.57389638
SVOC POHC Feed Rate								
SVOC POHC Emission Rate (nd = full detection limit (DL))	2224893.40	2224893.40	2224893.40	2224893.40	2224893.40	2224893.40	2224893.40	2224893.40
DE of SVOC POHC (nd = full DL)	10.9	10.9	5.3	12.2	12.4	11.5	17.3	12.8
SVOC POHC Emission Rate (nd = 0)	99.99951	99.99951	99.99976	99.99945	99.99944	99.99948	99.99922	99.99942
DE of SVOC POHC (nd = 0)	100.00000	100.00000	100.00000	100.00000	100.00000	99.99994	99.99991	100.00000
Trichloroethylene (TCE) Feed Rate								
Trichloroethylene Emission Rate (VOC Tenax [®])	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84
Trichloroethylene Emission Rate (VOC Anasorb [®])	NA	nd 11.63360249	0.437268483	1.059385255	1.496213005	E 8.650971119	nd 0.70745191	nd 4.788654383
Trichloroethylene Emission Rate (VOC Total w/nd = full DL)	—	nd 17.61668453	0.041692864	0.136204775	NA	nd 115.3462128	nd 45.98458054	nd 47.88681902
Trichloroethylene Emission Rate (VOC Total w/nd = 0)	—	nd 29.25028702	0.478961347	1.195590003	1.496213005	123.9971839	nd 46.69203245	nd 52.67547341
DE of Trichloroethylene (Tenax [®])	99.999373	99.99976	99.999943	99.99993	99.99919	99.999533	99.99962	99.999742
DE of Trichloroethylene (Anasorb [®])	—	99.999050	99.999998	99.999993	—	99.993779	99.997520	99.997417
DE of Trichloroethylene (Total w/nd = full DL)	—	99.998422	99.999974	99.999936	99.999919	99.993312	99.997482	99.997159
DE of Trichloroethylene (Total w/nd = 0)	—	100.000000	99.999974	99.999936	99.999919	99.999533	100.000000	100.000000
1,2 Dichlorobenzene Feed Rate								
Dichlorobenzene Emission Rate	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84
DE of Dichlorobenzene (nd = full DL)	nd	1	nd	0.5	nd	1.1	1.4	1.9
	99.99995	99.99995	99.99997	99.99994	99.99994	99.99992	99.99990	99.99994

Table 6-2. Summary of Calculated Waste Destruction Efficiencies for Demonstration Tests (Continued)

Test Number	1	2	3	4	5	6	7	8
Solar Input, kWh/hr	200	0	200	0	100	100	100	100
Stoichiometry	1.2	1.2	1.4	1.4	1.4	1.3	1.3	1.3
1,2 Dichlorobenzene Feed Rate								
1,2 Dichlorobenzene Emission Rate (VOC Tenax [®])	mg/hr	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84	1854077.84
1,2 Dichlorobenzene Emission Rate (VOC Tenax [®])	mg/hr	NA	0.067353442	nd	0.03783466	nd	0.07045191	nd
1,2 Dichlorobenzene Emission Rate (VOC Anasorb [®])	mg/hr	—	nd	17.61668453	nd	0.03783466	nd	45.98458054
1,2 Dichlorobenzene Emission Rate (VOC Total)	mg/hr	—	nd	29.25034437	0.099424385	nd	0.07566932	nd
1,2 Dichlorobenzene Emission Rate (VOC Total w/nd = 0)	mg/hr	—	—	0	0.067353442	0	0.162208675	0
DE of 1,2 Dichlorobenzene (Tenax [®])	%	—	99.999373	99.999996	99.999998	99.999991	99.999962	99.999742
DE of 1,2 Dichlorobenzene (Anasorb [®])	%	—	99.999050	99.999998	99.999998	99.993779	99.997520	99.997417
DE of 1,2 Dichlorobenzene (Total w/nd = full DL)	%	—	99.998422	99.999995	99.999996	99.993770	99.997482	99.997159
DE of 1,2 Dichlorobenzene (Total w/nd = 0)	%	—	100.000000	99.999996	100.000000	99.999991	100.000000	100.000000
Toluene Feed Rate								
Toluene Emission Rate (VOC Tenax [®])	mg/hr	—	741631.13	741631.13	741631.13	741631.13	741631.13	741631.13
Toluene Emission Rate (VOC Tenax [®])	mg/hr	NA	nd	11.63365984	0.64673004	0.151338639	0.089776032	1.261597805
Toluene Emission Rate (VOC Anasorb [®])	mg/hr	—	nd	17.61668453	nd	0.03783466	NA	nd
Toluene Emission Rate (VOC Total)	mg/hr	—	nd	29.25034437	0.678800983	0.189173299	0.089776032	116.6078106
Toluene Emission Rate (VOC Total w/nd = 0)	mg/hr	—	—	0	0.64673004	0.151338639	0.089776032	1.261597805
DE of Toluene (Tenax [®])	%	—	99.998431	99.999913	99.999980	99.999988	99.999830	99.999905
DE of Toluene (Anasorb [®])	%	—	99.997625	99.999996	99.999995	—	99.984447	99.993543
DE of Toluene (Total w/nd - full DL)	%	—	99.996056	99.999908	99.999974	99.999988	99.984277	99.993704
DE of Toluene (Total w/nd = 0)	%	—	100.000000	99.999913	99.999980	99.999988	99.999830	100.000000
Xylenes (Dimethylbenzene) Feed Rate								
Xylenes Emission Rate (VOC Tenax [®])	mg/hr	—	741631.13	741631.13	741631.13	741631.13	741631.13	741631.13
Xylenes Emission Rate (VOC Tenax [®])	mg/hr	NA	nd	11.63365984	nd	0.03783466	0.056109096	0.848945044
Xylenes Emission Rate (VOC Anasorb [®])	mg/hr	—	nd	17.61668453	nd	0.03783466	NA	nd
Xylenes Emission Rate (VOC Total)	mg/hr	—	nd	29.25028702	nd	0.07566932	0.056109096	64.51989213
Xylenes Emission Rate (VOC Total w/nd = 0)	mg/hr	—	—	0	0	0.056109096	0.050464463	64.51989213
DE of Xylenes (Tenax [®])	%	—	99.998431	99.999996	99.999995	99.999992	99.999993	99.999886
DE of Xylenes (Anasorb [®])	%	—	99.997625	99.999996	99.999995	—	99.984447	99.991415
DE of Xylenes (Total w/nd=full DL)	%	—	99.996056	99.999991	99.999990	99.999992	99.984440	99.991300
DE of Xylenes (Total w/nd=0)	%	—	100.000000	100.000000	100.000000	99.999992	99.999993	100.000000
Ethylbenzene Feed Rate								
Ethylbenzene Emission Rate (VOC Tenax [®])	mg/hr	—	741631.13	741631.13	741631.13	741631.13	741631.13	741631.13
Ethylbenzene Emission Rate (VOC Tenax [®])	mg/hr	NA	nd	11.63365984	nd	0.03783466	0.041145193	nd
Ethylbenzene Emission Rate (VOC Anasorb [®])	mg/hr	—	nd	17.61668453	nd	0.03783466	NA	nd
Ethylbenzene Emission Rate (VOC Total)	mg/hr	—	nd	29.25034437	nd	0.07566932	0.041145193	nd
Ethylbenzene Emission Rate (VOC Total w/nd=0)	mg/hr	—	—	0	0	0.041145193	0	0

Table 6-2. Summary of Calculated Waste Destruction Efficiencies for Demonstration Tests (Continued)

Test Number	1	2	3	5	6	7	8
Solar Input, kBtu/hr	200	0	200	0	100	100	100
Stoichiometry	1.2	1.2	1.4	1.4	1.3	1.3	1.3
DE of Ethylbenzene (Tenax [®])	—	99.998431	99.999996	99.999994	99.999995	99.999905	99.999354
DE of Ethylbenzene (Anasorb [®])	—	99.997625	99.999996	—	99.984447	99.993800	99.993543
DE of Ethylbenzene (Total w/ nd=full DL)	—	99.996056	99.999991	99.999994	99.984442	99.993704	99.992897
DE of Ethylbenzene (Total w/ nd=0)	—	100.000000	100.000000	99.999994	100.000000	100.000000	100.000000
Benzene Feed Rate							
Benzene Emission Rate (VOC Tenax [®])	mg/hr	741631.13	741631.13	741631.13	741631.13	741631.13	741631.13
Benzene Emission Rate (VOC Anasorb [®])	mg/hr	NA	0.179388277	0.098370116	0.153363385	nd	0.70745191
Benzene Emission Rate (VOC Total)	mg/hr	—	0.032070943	0.03783466	NA	nd	45.98458054
Benzene Emission Rate (VOC Total w/nd = 0)	mg/hr	—	0.21145922	0.136204775	0.153363385	nd	46.69203245
DE of Benzene (Tenax [®])	%	—	0	0.179388277	0.136204775	0	0
DE of Benzene (Anasorb [®])	%	—	99.998431	99.999976	99.999979	99.999976	99.999905
DE of Benzene (Total w/nd = full DL)	%	—	99.997625	99.999996	—	99.984447	99.993543
DE of Benzene (Total w/nd = 0)	%	—	99.996056	99.999971	99.999982	99.993704	99.992897
Carbon Tetrachloride Feed Rate							
Carbon Tetrachloride Emission Rate (VOC Tenax [®])	mg/hr	—	370815.57	370815.57	370815.57	370815.57	370815.57
Carbon Tetrachloride Emission Rate (VOC Anasorb [®])	mg/hr	NA	30.24751303	E 12.6501265	E 19.6742448	S 57.67312015	6.013368754
Carbon Tetrachloride Emission Rate (VOC Total)	mg/hr	—	nd	0.198855142	E 4.16185692	NA	nd
Carbon Tetrachloride Emission Rate (VOC Total w/nd = 0)	mg/hr	—	47.86419756	12.84898164	23.83610172	26.55782518	51.9979493
DE of Carbon Tetrachloride (Tenax [®])	%	—	30.24751303	12.84898164	23.83610172	26.55782518	6.013368754
DE of Carbon Tetrachloride (Anasorb [®])	%	—	99.991843	99.996589	99.992838	99.984447	99.99378
DE of Carbon Tetrachloride (Total w/nd = full DL)	%	—	99.995249	99.999946	99.998878	—	99.987086
DE of Carbon Tetrachloride (Total w/nd = 0)	%	—	99.987092	99.996535	99.993572	99.953341	99.985977
Pentachlorophenol (PCP) Feed Rate							
PCP Emission Rate	mg/hr	370815.57	370815.57	370815.57	370815.57	370815.57	370815.57
DE of PCP (w/nd = full DL)	%	99.997330	99.997330	99.997330	99.997330	99.997330	99.997330

Notes:

* SVOC includes 1,2 dichlorobenzene analyzed in SVOC sample

DE = Destruction Efficiency
 kBtu/hr = thousand British thermal units per hour
 NA = data not available
 nd = Non-detect
 VOC Anasorb[®] = Recovered from Anasorb[®]
 VOC Tenax[®] = Recovered from Tenax[®]

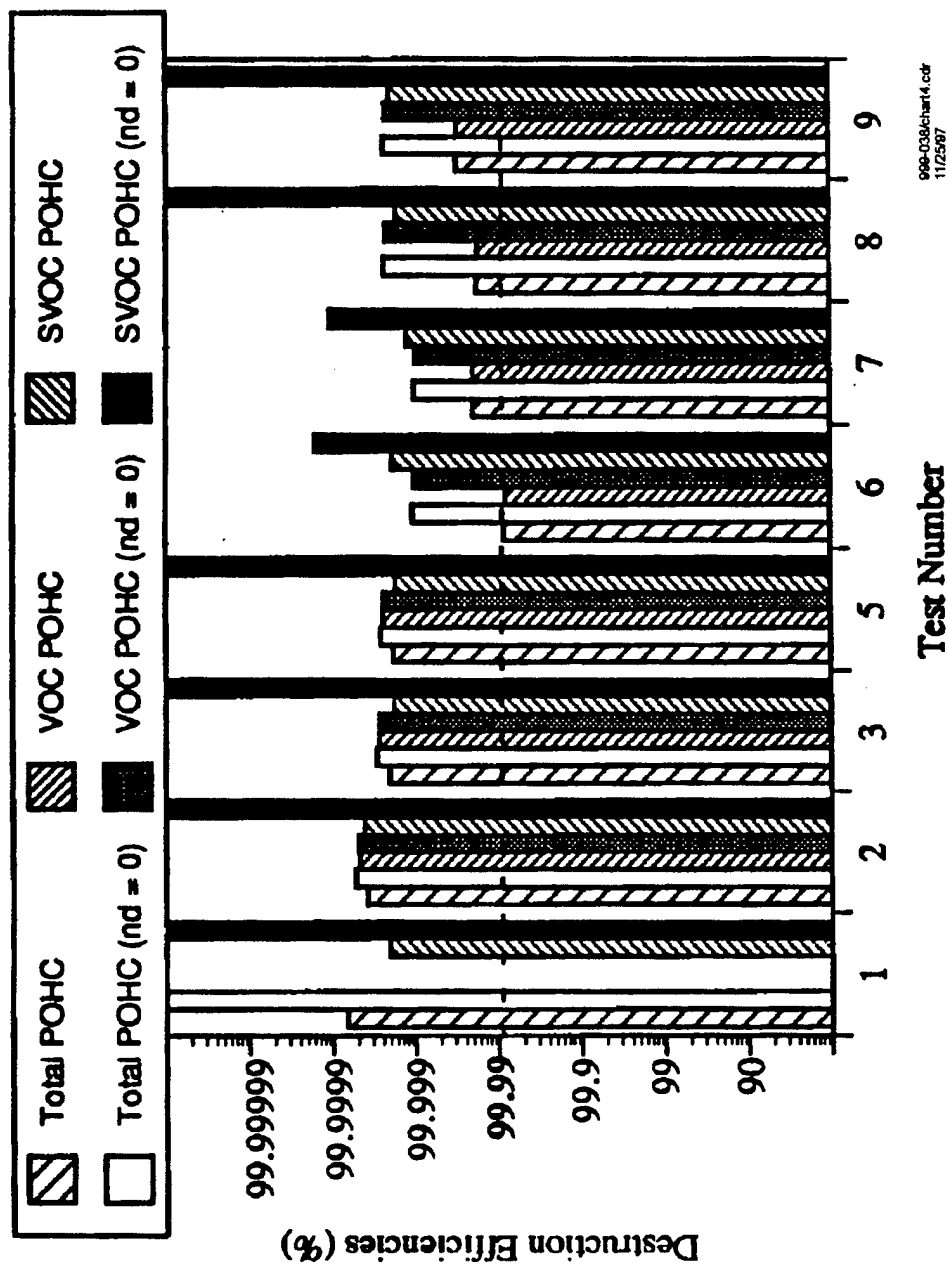


Figure 6-3. Solar Reactor Waste Destruction Efficiencies

non-detects set to equal the full detection limit; this DE range increased to 99.99991 to 100.00000 percent when concentrations of non-detects were set equal to zero.

Statistical analyses of the DE for total POHCs, VOC POHCs, SVOC POHCs and carbon tetrachloride were conducted. Carbon tetrachloride was selected from the VOC list because of its very low flammability. The statistical results are presented in Appendix F-1. The statistical analysis indicates that a process effect cannot be determined for total POHC, VOC POHC, and carbon tetrachloride DEs when concentrations of non-detects are set equal to the full detection limit or to zero. There is low confidence (80 percent) that SVOC POHCs are impacted by reactor stoichiometry. The statistical analysis indicates that DE increases only 36 percent when excess air is lowered from 40 to 20 percent. Statistical analyses also indicate no discernible effect of reactor exit gas temperature, cooling water heat extraction or reactor heat loss on the DEs for total POHCs, VOCs, and SVOCs.

Of all the VOCs, carbon tetrachloride was most often found above the detection limits. The destruction of carbon tetrachloride ranged from 99.95334 to 99.99653 percent with concentrations of non-detects set equal to the full detection limit, and ranged from 99.98445 to 99.99838 percent with concentrations of non-detects set equal to zero. Generally, this compound experienced the poorest destruction. Carbon tetrachloride was destroyed at 99.99 percent efficiency, with and without solar input, in three of the seven tests in which carbon tetrachloride data were collected, with non-detect concentrations set equal to the detection limit. The DE met the 99.99 percent criteria in six of seven tests when non-detect concentrations were set equal to zero.

The reactor destroyed PCP to non-detectable levels for all tests. The DEs, with concentrations of non-detects set equal to the detection limit, were 99.99585 to 99.99871 percent. Because analytical detection limits for PCP do not represent greater than 99.99 to 99.999 percent DE, a solar or stoichiometry effect on PCP destruction could not be determined. 1,2-DCB was detected in two tests at levels just above the detection limit. The DE of 1,2-DCB for these two detections were 99.99990 and 99.99992 percent. The full range of DE for 1,2-DCB was from 99.99990 to 99.99997 percent for all tests, assuming concentrations of non-detects were at the detection limit. These results suggest the reactor was effective at destroying PCP and 1,2-DCB.

The reactor met the goal of 99.99 percent destruction of total POHCs in eight of the nine tests. Significant effects of operating conditions on DE were not evident. In some cases, this may be caused by the high detection limits or the variability in detection limits as discussed in Section 4. It appears the reactor was effective at destroying the surrogate waste even at low temperature provided stable combustion is occurring.

6.3.2 *Products of Incomplete Combustion*

Another objective of the demonstration was to achieve low levels of PICs and show that the compounds of greatest concern, based on toxicity, are at or below levels typically emitted from hazardous waste incinerators.

6.3.2.1 *PCDD/PCDF*. PCDD/PCDF production was required to meet or exceed the soon to be promulgated hazardous waste combustion standards for 2,3,7,8-TCDD TEQ. This standard could be as low as 0.2 ng/dscm (dry, 7 percent O₂) but may be raised to 0.4 ng/dscm (dry, 7 percent O₂).

As part of the solar reactor demonstration, PCDD/PCDF concentrations were measured in the flue gas upstream of the scrubber for Tests 2, 6, 7, 8, and 9. Results ranged from 5.8 to 23.7 ng/dscm (dry, 7 percent O₂). Tests 2 and 9 were conducted at a 1.2 stoichiometry (20 percent excess air) with 0 and 200 kBtu/hr solar input, respectively, to identify the potential impact of sun on PCDD/PCDF formation. To determine whether a significant difference in PCDD/PCDF concentrations exists, PCDD/PCDF concentrations were also measured for the three replicate tests (Tests 6, 7, and 8) operated at 1.3 stoichiometry and 100 kBtu/hr solar input. The 2,3,7,8-TCDD TEQs for the selected tests are presented in Table 6-3 and PCDD/PCDF summary data are presented in Appendix A.

The program objective was to limit formation of PCDD/PCDF to a 2,3,7,8-TCDD TEQ below 0.2 or 0.4 ng/dscm (dry, 7 percent O₂). Concentrations generated were an order of magnitude higher than the objective during all tests. Because flue gas sampling upstream of the scrubber was necessary, the reactor flue gas ducting was externally heated to between 150°C (300°F) and 260°C (500°F) to avoid HCl condensation. The duct was heated from the boom-mounted quench chamber to the ground-based sampling ports, which was a distance of 80 to 100 feet. This length provided 3 to 5 seconds of residence time for the generation of PCDD/PCDF in what is known to be a probable temperature window for PCDD/PCDF formation. It was desirable to measure flue gas composition upstream of the scrubber to be able to determine a solar impact on waste destruction. However, in the ultimate application of this technology, flue gas sampling upstream of the scrubber would not be necessary; therefore, the flue gas from the reactor could be completely quenched to minimize the potential downstream formation of PCDD/PCDF.

Table 6-3. Toxic Equivalents for PCDD/PCDF Analyses

Test No.	Stoichiometry	Solar Input kBtu/hr	2,3,7,8-TCDD TEQ ng/dscm (7% O ₂)
2	1.2	0	23.7
6	1.3	100	15.4
7	1.3	100	12.2
8	1.3	100	5.8
9	1.2	200	6.4

Notes:

kBtu/hr = thousand British thermal units per hour
 ng/dscm = nanograms per dry standard cubic meter
 TEQ = toxic equivalents

PCDD/PCDF can form by two different mechanisms; (1) incomplete combustion of chlorinated aromatics, or by (2) chemical condensation of a variety of chlorinated organic radical species in exhaust from combustion of chlorinated organics (as noted in C.R. Dempsey and E.T. Oppelt, "Incineration of Hazardous Waste: A Critical Review Update," Air and Waste, Vol. 43, pp 25-72, January, 1993). The prolonged residence times at cooler temperatures than the reactor, and with ample metal surface, would allow a condensation of fragments to form the larger PCDD and PCDF molecules by mechanism 2.

The effect of solar insolation on the 2,3,7,8-TCDD TEQ formation was determined utilizing a t-test statistical analysis. The TEQ for Test 9 was compared to the mean TEQ for the triplicate tests (Tests 6, 7, and 8). The triplicate tests mean TEQ and standard deviation (S) are:

$$\text{mean TEQ} = 11.13 \text{ ng/dscm (dry, 7 percent O}_2\text{)}$$

$$S = 4.89 \text{ ng/dscm (dry, 7 percent O}_2\text{)}$$

On applying the t-test with a 95 percent confidence level and two degrees of freedom, the confidence interval is -1.02 to 23.3 ng/dscm. For Test 9 with on-sun conditions, the TEQ of 6.34 ng/dscm is not significantly different than the mean for the triplicate on-sun tests. However, the 23.7 ng/dscm TEQ for Test 2 with off-sun conditions is just outside the confidence interval. From this limited sample set, the determination of solar insolation effects on PCDD/PCDF formation is inconclusive. Additional test data would be desirable; for example, repetition of Tests 2 and 9 could establish the mean TEQ values for each of these operating modes to verify the analysis.

A comparison of the upstream and solar reactor 2,3,7,8-TCDD-TEQs with those from other hazardous waste units is presented in Figure 6-4. The TEQ results were retrieved from a database of trial burn reports for boilers and industrial furnaces firing hazardous waste ("Technical Support Document for HWC MACT Standards, Volume II: HWC Emissions Data Base," USEPA, November 1995). The figure indicates that levels of PCDD/PCDF formed in the solar reactor system are comparable to those levels reported by commercial incinerators in trial burn test reports. The TEQ levels from trial burn reports are based on units that do not feed PCDD/PCDF and are measured upstream of the exhaust gas subsystem.

6.3.2.2 VOCs and SVOCs. VOCs and SVOCs were required to be produced at or below levels typically emitted from hazardous waste incinerators to meet test objectives.

The formation of VOC/SVOC PICs in the reactor was determined by analyzing the flue gas samples for an extended list of compounds (see Appendix B). The analytical results are presented in Appendices A and B. Table 6-4 summarizes the SVOC PICs detected during the tests, including concentration, test number, and test conditions.

Comparable SVOC PIC results were retrieved from a database of trial burn reports for boilers and industrial furnaces firing hazardous waste ("Technical Support Document for HWC MACT Standards, Volume II: HWC Emissions Data Base," USEPA, November 1995). SVOC PIC data from these trial burn reports are compared in Figure 6-5 with the solar reactor concentrations

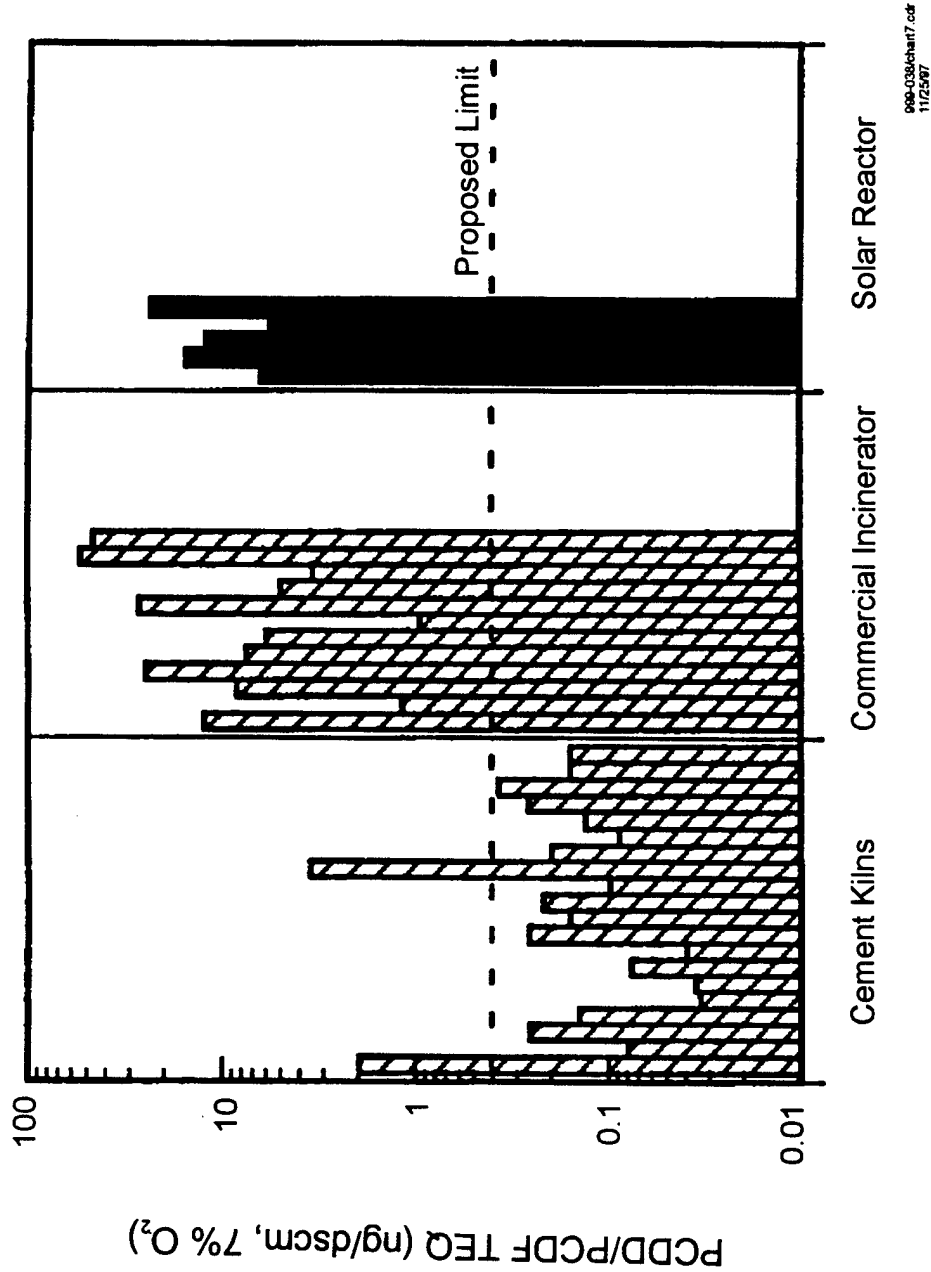


Figure 6-4. Comparison of the Solar Reactor 2,3,7,8-TCDD TEQ Concentrations with Other Hazardous Waste Combustor TEQ Concentrations Measured Upstream of the Exhaust Gas Subsystem

Table 6-4. Non-PCDD/PCDF SVOC Formed in Solar Detoxification Tests

Compound	Concentration, ng/dscm (7% O ₂)	Test No.	Conditions
Hexachlorobenzene	51,000	Average over all tests	—
Pentachlorobenzene	90,300	7	100 kBtu insolation 1.3 stoichiometry
1,2,4-trichlorobenzene	14,300	6	100 kBtu insolation 1.3 stoichiometry

Notes:

kBtu = thousand British thermal units
ng/dscm = nanogram per dry standard cubic meter

represented by actual detected levels or the detection limit. The trial burn report emissions for hexachlorobenzene and pentachlorobenzene are from stack sampling downstream of the exhaust gas subsystem. Bis(2-ethylhexyl)phthalate was not detected in any sample so the average detection limit of 14,350 ng/dscm (dry, 7 percent O₂) was presented in the figure. SVOC PAHs were not detected; the maximum PAH detection limit was 21,500 ng/dscm (dry, 7 percent O₂).

The formation of VOC PICs in the reactor is compared to reported concentrations upstream of the exhaust gas subsystem for trial burns. VOC PIC data from the trial burn reports are presented in Figure 6-6 and compared to the solar reactor concentrations represented by actual detected levels or the detection limit. Most of the solar reactor VOC PIC concentrations varied and had wide ranges in non-detects. The solar reactor data presented in Figure 6-6 were selected from Test 3, with 200 kBtu/hr solar input and a 1.4 stoichiometry. This figure shows that the reactor generates PICs at levels comparable to commercial incinerators.

6.3.3 Other Pollutants

CO, NO_x, and THC were also required to be produced at or below levels typically emitted from hazardous waste incinerators. There are specific hazardous waste combustion standards for CO and THC, while NO_x standards may be imposed on a site-by-site basis. Specific demonstration objectives for the compounds were:

- CO emissions were required to meet or exceed the hazardous waste combustion standard of CO 100 ppmv (dry, 7 percent O₂).
- NO_x emissions were required to be below that of other conventional hazardous waste incineration technologies. Incinerators are not specifically required to meet a standard for NO_x emissions unless the area has been designated a nonattainment

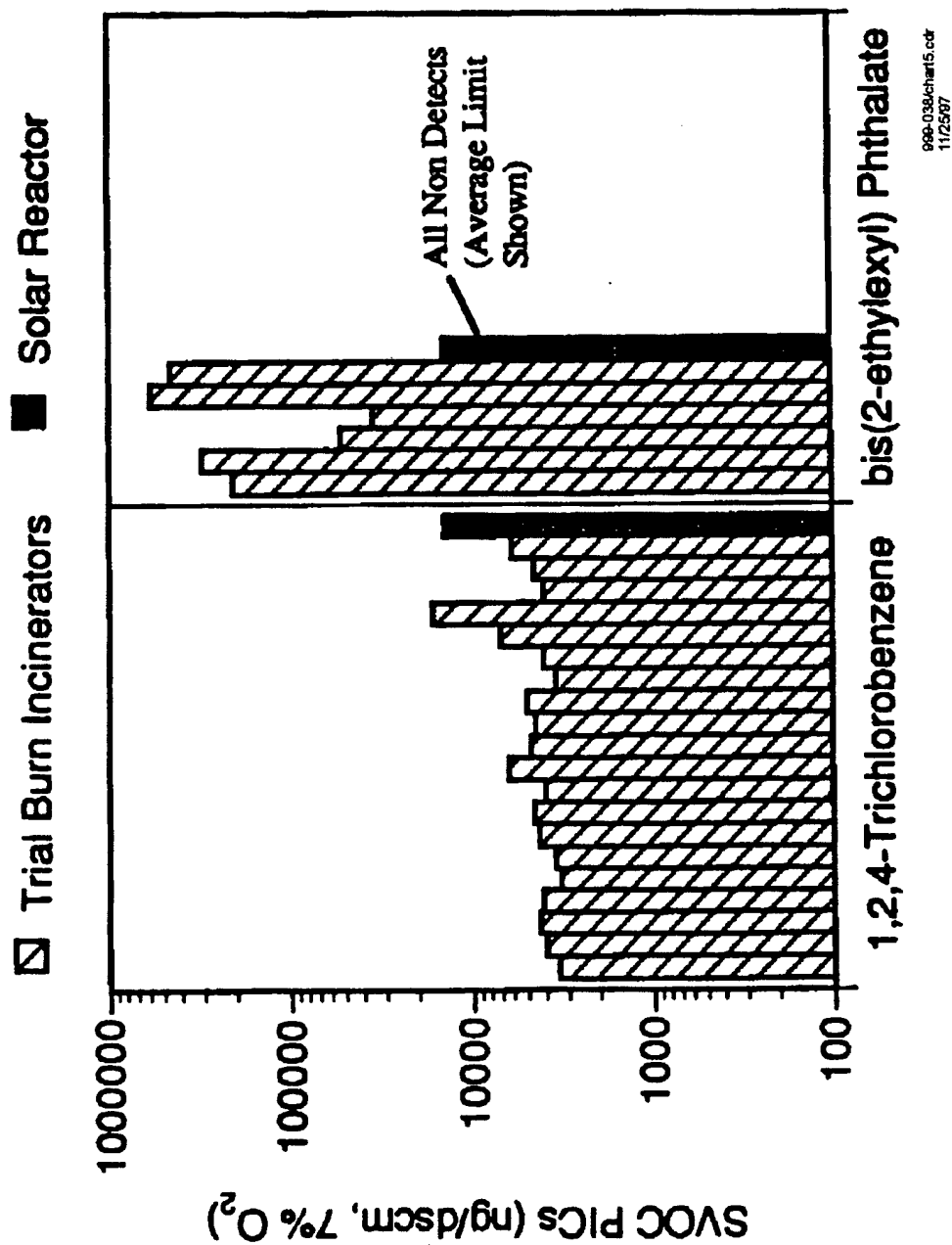


Figure 6-5. Comparison of the Solar Reactor SVOC PIC Concentrations with Other Hazardous Waste Combustor PIC Concentrations Measured Upstream of the Exhaust Gas Subsystem

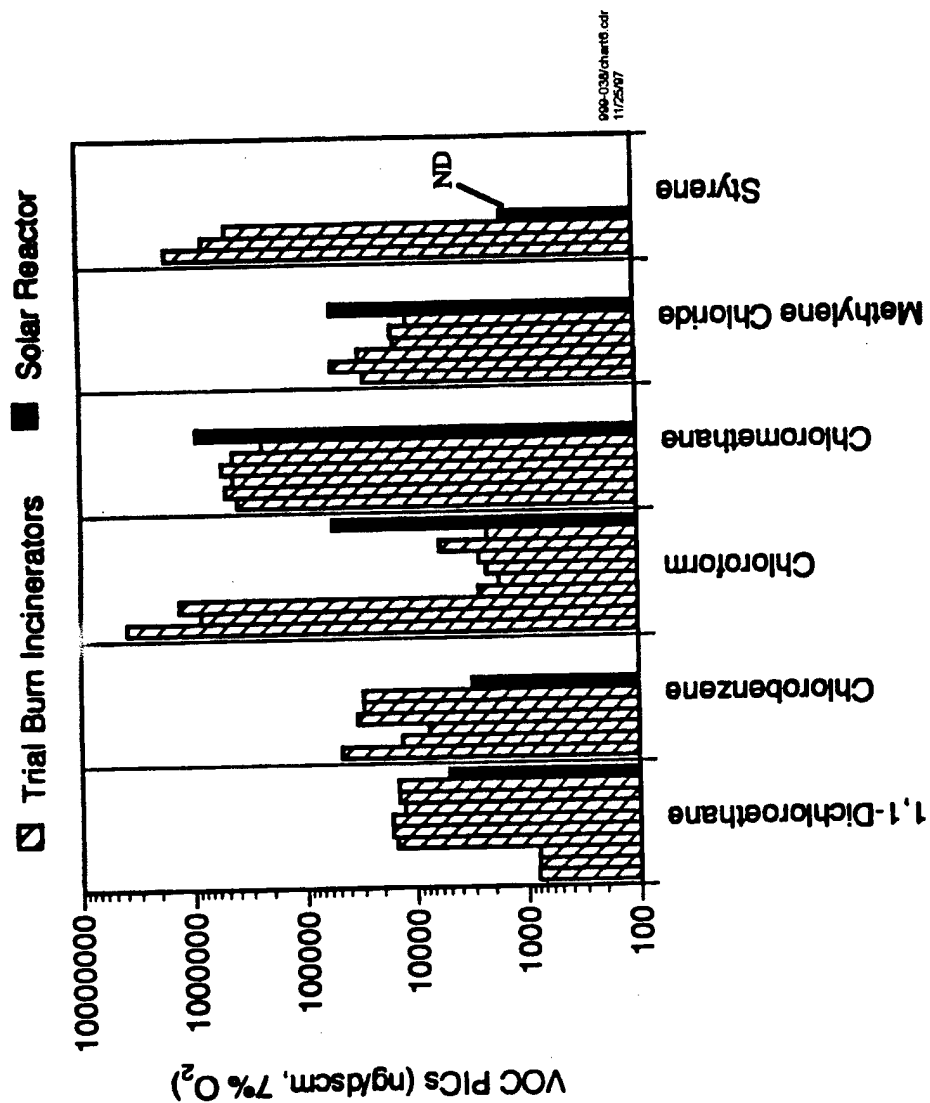


Figure 6-6. Comparison of the Solar Reactor VOC PIC Concentrations with Other Hazardous Waste Combustor PIC Concentrations Measured Upstream of the Exhaust Gas Subsystem

area under the Clean Air Act (CAA)¹⁴. The NO_x emissions of the solar reactor can be compared to the proposed medical waste standard of 210 ppmv (dry, 7 percent O₂) and municipal waste NSPS of 180 ppmv (dry, 7 percent O₂).

- THC emissions were required to meet or exceed the hazardous waste combustion standards of 10 ppmv (dry, 7 percent O₂).

CEMS recorded exhaust gas concentrations of CO, NO_x, THC, CO₂ and O₂. Sulfur dioxide (SO₂) was not monitored. All CEMS results, except HCl, were recorded upstream of the flue gas scrubber and stack; HCl emissions were recorded at the stack. The average CEMS data with standard deviation, corrected to 7 percent O₂, are summarized in Table 6-5 for each test. Full CEMS data logs and test summary tables are presented in Appendices A and H. The results for the three criteria pollutants of concern are discussed and compared to these performance objectives in the following paragraphs.

6.3.3.1 Carbon Monoxide. As shown in Table 6-5, the results of the test series indicate that CO production varied from 12.28 ppmv to 673.13 ppmv during reactor operation. Highest CO generation occurred during Test 4, which had an unstable flame condition. However, the repeat condition (Test 5) did not indicate similarly high CO levels. In general, the variability in CO generation from test to test did not correlate well with operating conditions. This behavior suggests that mixing between the combustion air and the surrogate waste may have been unsatisfactory during certain run conditions or that the burnout of CO was quenched in the water-cooled entrance region. Streams of cooler gases along the water-cooled wall could exit the reactor quickly and not experience sufficient residence time for CO burnout. When operating without solar insolation, an asymmetrical flame was seen during several tests. Inspection of the injector nozzle showed a buildup of fine solids at the nozzle tip that could have contributed to the asymmetrical flame behavior.

Non-linear statistical analysis suggests, with limited confidence (greater than 88 percent), that raising the reactor stoichiometry (excess air level) may increase CO production levels. This operation would be consistent with reducing the flame temperature and shortening residence time. In general, this analysis predicts that the reactor should generate from 37 to 252 ppmv CO (dry, 7 percent O₂) over the stoichiometry range of 1.2 to 1.4, as shown in Figure 6-7.

The two tests (1 and 9), conducted at operating conditions of low stoichiometry (1.2) and high solar insolation (200 kBtu/hr), produced around 54 ppmv CO (dry, 7 percent O₂), which meets the 100 ppmv (dry, 7 percent O₂) CO emissions objective; whereas over the range of conditions studied, the average CO production of 181 ppmv is above the standard. Optimization of operating conditions against all performance criteria would thus be required to ensure the reactor would meet the CO criteria during standard operations.

¹⁴ Total NO_x emissions are regulated under Title I of the 1990 CAA Amendments for the control of smog or ozone in nonattainment areas. In general, the NO_x standard in nonattainment areas is placed on units processing greater than 50 million British thermal units per hour (mmBtu/hr). Smaller units are not regulated by Federal CAA standards at this time, but local districts such as Southern California Air Quality Management District can impose NO_x limits that are more stringent than Federal standards.

Table 6-5. Summary of Corrected CEMS Data for the Reactor Operation Conditions

Test No.	Test ID	Date	Test Start Time	Test Stop Time	Waste Heat Input (Btu/hr)	LPG Pilot Heat (Btu/hr)	Solar Heat Input (Btu/hr)	Reactor Stoich.	Reactor Gas Exit Temp. "A and B" (°F)	Total Heat Input (Btu/hr)	Oxygen (dry, 7% O ₂)		Carbon Dioxide (dry, 7% O ₂)	
											Average (%)	Std. Dev. (%)	Average (%)	Std. Dev. (%)
1	062097001	6/20/97	11:15 AM	12:02 PM	170,000	30,000	200,000	1.20	1,172	400,000	4.77	0.26	16.74	0.38
2	062097002	6/20/97	4:35 PM	6:35 PM	170,000	30,000	0	1.20	917	200,000	4.77	0.41	16.24	0.42
3	062197001	6/21/97	12:05 PM	2:30 PM	170,000	30,000	200,000	1.40	1,159	400,000	7.04	0.06	12.83	0.22
4	062197002	6/21/97	3:45 PM	5:25 PM	170,000	30,000	0	1.40	960	200,000	7.13	0.16	12.98	0.25
5	062397002	6/23/97	2:25 PM	4:25 PM	170,000	30,000	0	1.40	970	200,000	6.74	0.08	14.60	0.11
6	062697001	6/26/97	9:45 AM	11:45 AM	170,000	30,000	100,000	1.32	1,100	300,000	6.24	0.10	11.96	0.13
7	062697002	6/26/97	12:20 PM	2:03 PM	170,000	30,000	100,000	1.33	1,088	300,000	6.39	0.10	11.96	0.33
8*	062797001	6/27/97	8:55 AM	10:45 AM	170,000	30,000	100,000	1.31	1,097	300,000	6.16	0.08	13.85	0.25
9*	062897001	6/28/97	8:20 AM	10:25 AM	170,000	30,000	200,000	1.20	1,190	400,000	4.90	0.15	13.52	0.15

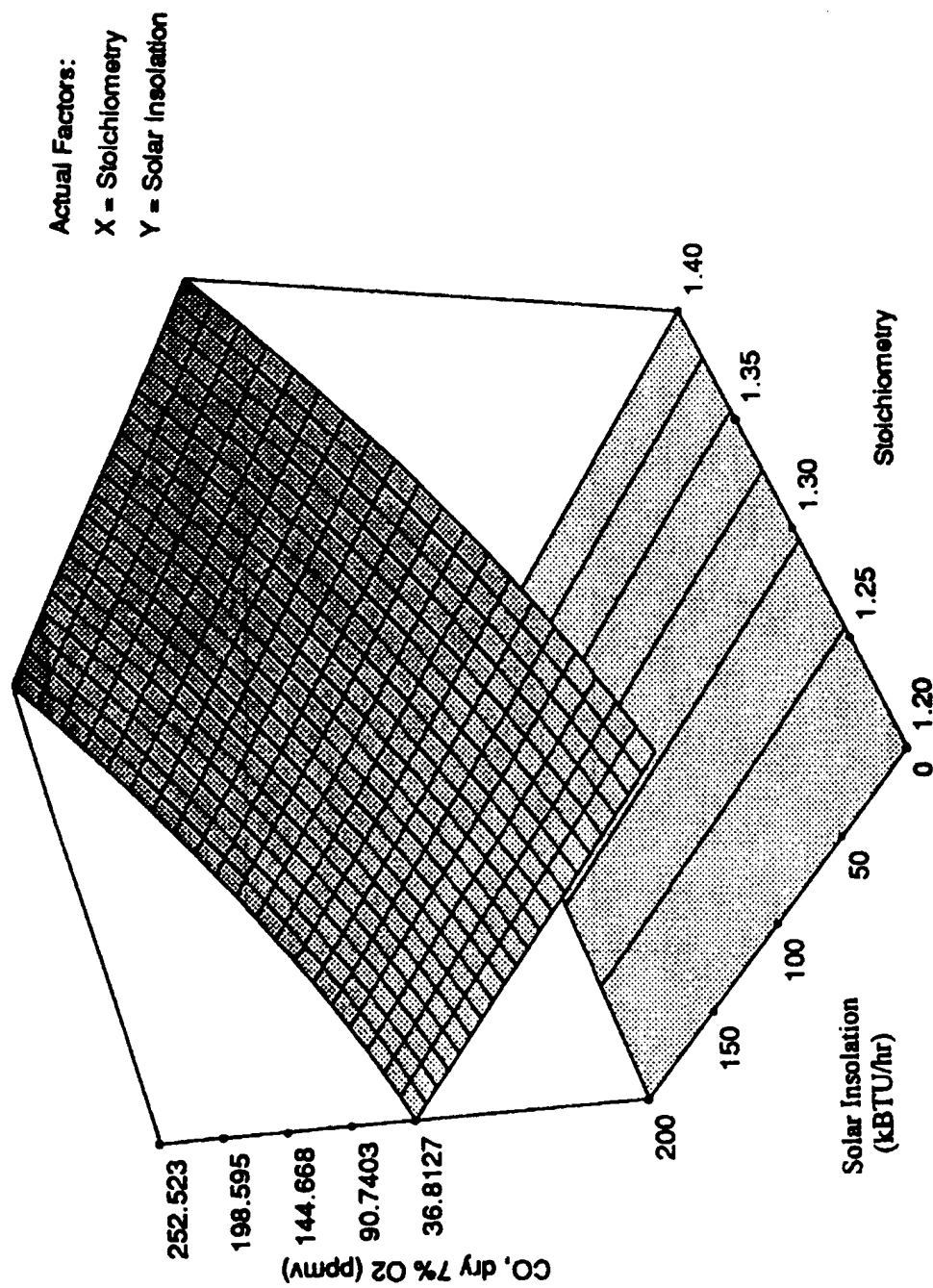
Table 6-5. Summary of Corrected CEMS Data for the Reactor Operation Conditions (Continued)

Test No.	Test ID	Date	Test Start Time	Oxides of Nitrogen (dry, 7% O ₂)			Carbon Monoxide (dry, 7% O ₂)			Hydrochloric Acid (wet, 7% O ₂)			Total Hydrocarbon (wet, 7% O ₂)		
				Average (ppmv)	Std. Dev. (ppmv)		Average (ppmv)	Std. Dev. (ppmv)		Average (ppmv)	Std. Dev. (ppmv)		Average (ppmv)	Std. Dev. (ppmv)	
1	062097001	6/20/97	11:15 AM	62.32	10.30		57.94	59.44		23.09	12.22		0.72	0.30	
2	062097002	6/20/97	4:35 PM	44.95	3.55		12.28	11.81		24.54	18.93		0.36	0.58	
3	062197001	6/21/97	12:05 PM	44.32	1.21		176.00	48.65		20.51	21.83		0.01	0.19	
4	062197002	6/21/97	3:45 PM	43.94	14.80		673.13	640.13		18.48	18.41		1.00	8.83	
5	062397002	6/23/97	2:25 PM	38.96	3.61		71.60	25.73		30.20	27.74		0.54	0.21	
6	062697001	6/26/97	9:45 AM	38.68	1.69		171.47	80.87		0.00	2.80		1.99	0.82	
7	062697002	6/26/97	12:20 PM	14.06	2.61		378.22	143.39		4.52	6.05		2.23	1.20	
8*	062797001	6/27/97	8:55 AM	48.51	15.26		41.45	1.70		1.08	0.26		1.19	3.22	
9*	062897001	6/28/97	8:20 AM	1.77	0.43		50.19	14.29		2.60	0.44		0.15	3.00	

Notes:

* CEMS Computer DAS out-of-service, retrieved data from Control Computer DAS

Btu/hr = British thermal units per hour
 ppmv = parts per million volume
 Std. Dev. = standard deviation
 stoich. = stoichiometry



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Figure 6-7. Statistically Generated Response of Average Flue Gas CO Levels Versus Solar Input and Stoichiometry

6.3.3.2 Oxides of Nitrogen. Because the reactor operated at low reactor temperatures, the formation of NO_x was substantially reduced. The results showed low NO_x emissions across all operating conditions indicating that stoichiometry or solar insolation did not significantly impact NO_x formation. NO_x levels for each test are presented in Figure 6-8. The average NO_x formation was 43.6 ppmv (dry, 7 percent O₂), which is well below the NSPS of 180 ppmv (dry, 7 percent O₂) and also below the medical waste standard of 210 ppmv (dry, 7 percent O₂).

6.3.3.3 Total Hydrocarbon. During the reactor tests, THC levels were measured upstream of the scrubber. The THC levels ranged from 0.01 to 2.23 ppmv over the nine tests conducted. THC levels for all tests, which were measured upstream of the scrubber, were significantly below the 10 ppmv (dry, 7 percent O₂) hazardous waste combustion standard for stack emissions.

Statistical analysis of THC emission results indicates non-normally distributed error in the normal plot of residuals presented in Appendix F-1; therefore the statistical model is potentially invalid for THC emissions. Other transformation options were investigated to correct the non-normality of the error term. Better normality of the error term was achieved with other transformations, however, no significant effect of operating conditions on the THC emissions was inferred from these analyses.

6.3.4 Stack Hydrochloric Acid Emissions

The demonstration objective for HCl production was to ensure HCl emissions from the exhaust scrubbing system met the regulatory standards of 50 ppmv (dry, 7 percent O₂).

HCl emissions data collected with the CEMS were presented previously in Table 6-5. The results indicate that the scrubber was capable of reducing the flue gas HCl concentrations from 2.76 percent levels (wet, uncorrected) to an average stack emission of 18 ppmv (wet, uncorrected). The scrubber was effective at removing over 99.9 percent of the incoming HCl and met the manufacturer's specification for 99.75 percent removal. The average HCl concentration for all tests conducted was 14 ppmv (wet, 7 percent O₂) with a test-to-test standard deviation of 11 ppmv. HCl emissions performance exceeded the goal of 50 ppmv HCl. Average HCl emissions for each test are presented in Figure 6-9.

6.4 Data Quality Achieved

This section provides a discussion of the program field data quality. Data quality objectives were presented previously in Section 5.

6.4.1 Precision

An indication of process precision can be derived from process monitoring results, such as reactor gas compositions and gas temperatures, for repeated test conditions. The flue gas O₂ and CO₂ concentrations provided information about the variability of the input streams such as combustion air and chemical feed. The precision of the operating conditions, as indicated by RSD for O₂ and CO₂ flue gas concentrations, was 2 and 9 percent, respectively, averaged over the triplicate tests (Tests 6, 7, and 8). Variability of the O₂ and CO₂ concentrations during each

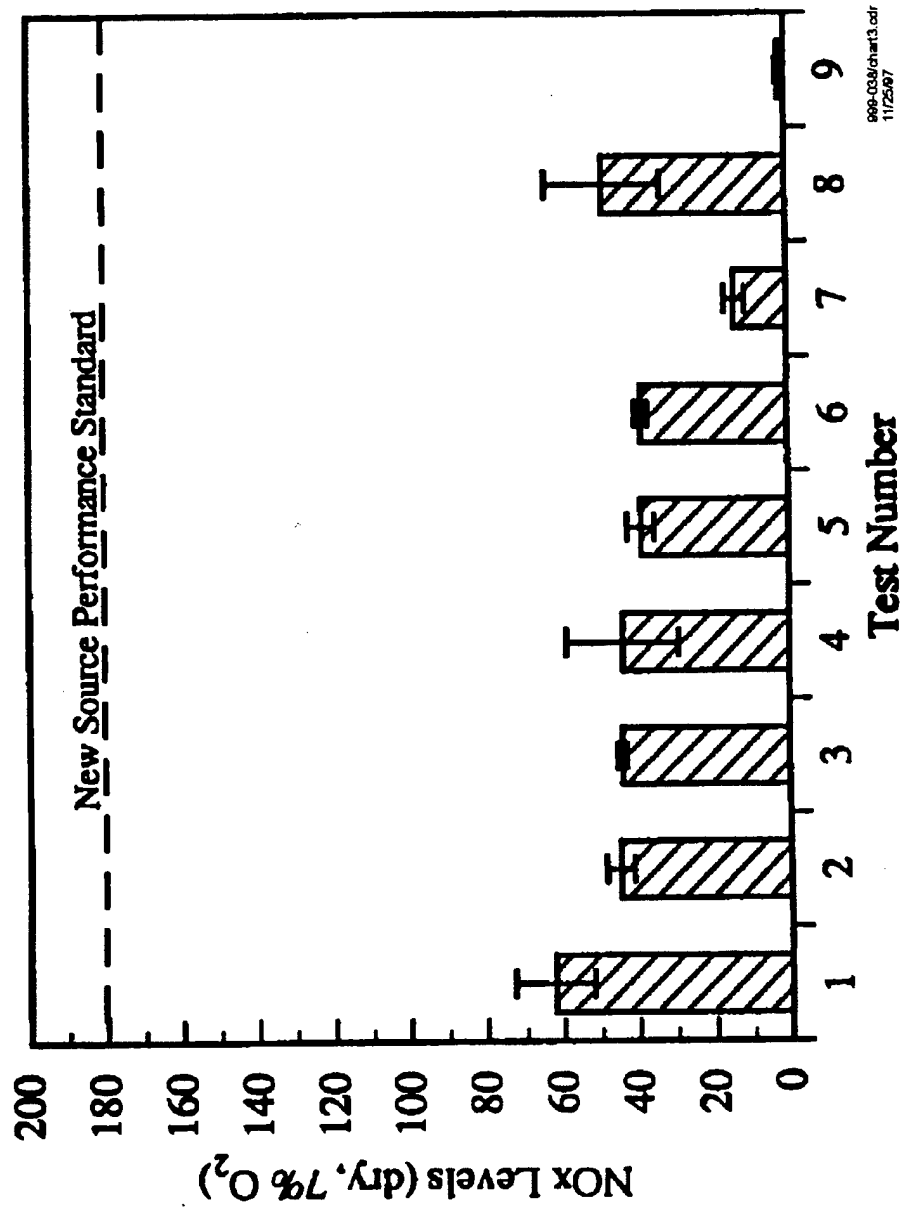


Figure 6-8. Average and Standard Deviation of NO_x Levels Generated During Each Test Condition

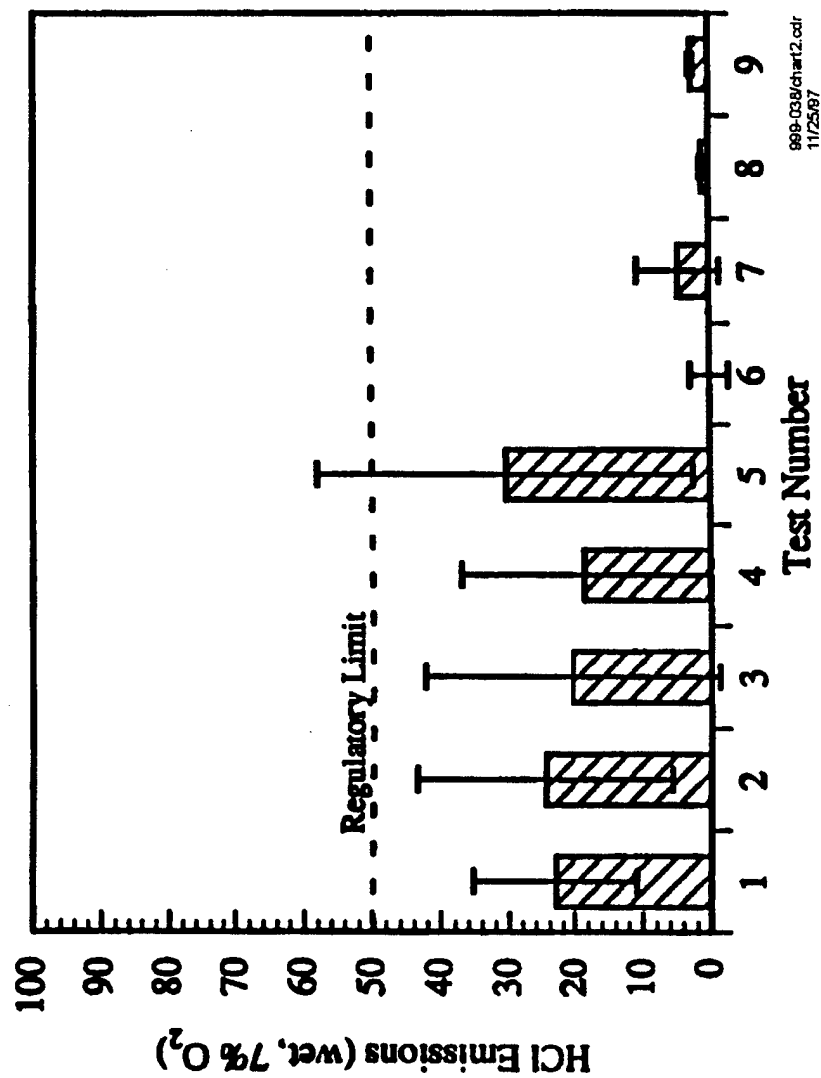


Figure 6-9. Average and Standard Deviation of HCl Emission for Each Test Condition

of the triplicate tests was less than 2 percent. Without accounting for the variability of the analytical instruments, these data show that the reactor processing conditions were maintained during a single test period with good precision of less than 2 percent RSD, and the process conditions were repeatable with good precision of less than 10 percent RSD.

The reactor exit gas temperatures provide an additional indication of process precision. Exit gas temperatures were measured in two of the four reactor exhaust ducts. The RSD of exit gas temperatures during the triplicate tests was between 0.7 and 1.4 percent. The repeatability of exit gas temperatures for the triplicate tests was very good with a standard deviation of 0.5 and 0.8 percent for exit gas temperature "A" and "B", respectively. The gas temperature and concentration data used to indicate the process precision are provided in Tables 6-1 and 6-2.

The precision objectives for the VOCs were met for the internal standards (or surrogate standards) and the pre-spike compound benzene-d₆. The RPD for the recovery of the pre-spike surrogate *cis*-1,2-dichloroethene was 1,001 percent for the Tenax[®] and 69 percent for the Anasorb[®]. As discussed in Section 4, the imprecision in the Tenax[®] analysis may be partially due to the bag dilution analytical methodology utilized. The analytical precision objectives were met for both the SVOC and PCDD/PCDF analysis.

The statistical analysis results, which implicitly account for overall precision, are presented in Appendix F.

6.4.2 Accuracy

Analytical accuracy and precision for each of the methods is described in detail in Appendix G1. The SVOC, VOC, and PCDD/PCDF analytical accuracy was evaluated based on internal and pre-spike surrogate recoveries. The pre-spike surrogates were spiked in the respective resins prior to sample collection and the internal standards or surrogates were added to the sample just prior to analysis. The VOC accuracy appeared to be impacted by the high HCl concentrations in the reactor flue gases and the high dilution levels required to mitigate the impacts of high HCl concentrations on the analytical methods. The recoveries of *cis*-1,2-dichloroethene were most affected. Recoveries for this polar compound varied from 36 to 3,860 percent. The recovery objectives were met for the internal standards with the Tenax[®] sample and five of the seven Anasorb[®] samples. Overall, the Tenax[®] samples appeared to be less affected by the high HCl concentrations than the Anasorb[®] samples.

All accuracy objectives were met for the SVOC and the PCDD/PCDF samples; however, the dilution ratios decreased the sensitivity and increased the actual detection limits of the SVOC analysis.

6.4.3 Representativeness

To maximize representativeness, samples were taken during normal operation of the process and testing was suspended if the process deviated from normal operation as judged by the Principal Investigator.

6.4.4 Completeness

All of the test conditions were achieved and all samples required for the final test matrix (Table 3-2) were completed.

6.4.5 Comparability

For the purpose of this screening study, the PIC emissions for a selected set of operating conditions and a select number of compounds were compared with emissions from hazardous waste incinerators. This comparison is preliminary in nature since triplicate measurements that provide process repeatability were not performed for each condition. A discussion of this comparison is included in Paragraph 6.3.1, and shown in Figures 6-4, 6-5, and 6-6.

6.5 Overall Technology Evaluation

This section provides an evaluation of the design aspects of the as-tested solar detoxification system and identifies a number of recommended changes for future installations. This section also provides a comparative evaluation of the various aspects of this solar technology against the more classical technologies being used for the destruction of organic compounds found in contaminated soils and other waste.

6.5.1 System Design Evaluation

Testing of the solar detoxification system demonstrated the capability to integrate solar concentrator and thermal waste treatment technologies. The reactor performed effectively, achieving greater than 99.99 percent DE for chlorinated and aromatic hydrocarbon surrogate wastes (with the exception of carbon tetrachloride), even under low temperature [480°C (900°F) to 650°C (1,200°F)] conditions. However, the system could not operate over the intended range of operating conditions due to flame instability problems. Limitations experienced during the testing, such as flame instability that required continuous use of the pilot flame, lower stoichiometries and lower reactor temperatures, prevented clear demonstration of all of the features in the system design. This paragraph identifies development issues and recommendations that would allow optimization of the solar detoxification process.

6.5.1.1 Reactor Thermal Design. The reactor operation showed no problems with integration of solar heat input into conventional waste thermal treatment. Further developments are necessary to maximize the benefits of the solar heat input and to stabilize the liquid waste flame over a wider operating range of waste feed rate and stoichiometry.

Because solar energy is effective in heating solid surfaces, it is reasonable to consider replacing the water-cooled reactor surfaces with insulated refractory walls. By eliminating the water-cooled walls, the solar input would create hot-walled surfaces in the flame region, which would stabilize the flame and establish more uniform gas temperatures. This solar reactor program demonstrated that it was possible to stabilize the waste combustion with solar input with the LPG pilot flame on. However, the stabilization occurred downstream of the burner in the refractory region, which was kept hot by the solar input. Performance under this condition was

poor because combustion occurred in batches near the exit of the reactor, which further supports the concept of placing refractory at the reactor entrance. By installing refractory in the entrance region, solar insolation could provide the initiating heat to stabilize combustion and would eliminate the need for an LPG pilot flame. Also, allowable waste feed would likely increase dramatically.

6.5.1.2 Burner Design. During a single 2-hour test, CO levels dropped below 100 ppmv for several minutes and then jumped to over 1,000 ppmv for several minutes. The highly variable CO emissions that occurred from test to test may have resulted from poor liquid waste atomization or mixing. Further development of the liquid waste injection and burner design may be necessary to optimize the reactor performance. During off-sun conditions, asymmetrical flames were observed that may have been caused by poor waste flammability, atomizing nozzle performance, or lack of combustion air flow uniformity. The waste flammability, combined with the flame destabilizing conditions, such as cold reactor walls in the reactor entrance, are suspected to be the cause of variable CO emissions. Inspection of the atomizing nozzle showed small deposits that also may have contributed to the high variability in CO emissions.

Increasing the use of refractory and eliminating or reducing the water cooling could lead to higher temperatures in the flame region and increase thermal NO_x formation. Because NO_x levels were relatively low, additional NO_x formation may be acceptable in order to optimize reactor operation and waste destruction. To minimize NO_x formation, air injection downstream of the entrance region could be considered to moderate the gas temperature.

6.5.1.3 Cooling Systems. Potential advantages of eliminating water cooling systems include reducing water usage; eliminating large water tanks, pumps, and coolers; and simplifying the reactor design and operation. Another significant advantage of eliminating the water-cooled wall would be the elimination of condensation in the reactor at startup and shutdown. Condensation drips on the quartz window when the reactor is in the stow position. Eliminating the condensation would significantly help to keep the window clean, thereby simplifying daily maintenance of the solar reactor.

If cooling of reactor components is required, the use of regenerative or non-regenerative air cooling should be considered. Regenerative air cooling would utilize the combustion air to cool components before being fed to the burner. Non-regenerative cooling would use excess air to cool the critical components. This excess air would then be released from the reactor.

6.5.1.4 Reactor Window. Generally, few problems were experienced with the 18-inch diameter quartz window in the reactor. During normal on-sun testing, the window remained clean. When nearing the stability limit of the flame, the window would become sooty under off-sun conditions. The soot would then disappear after the flame burned clean again. With on-sun conditions, the soot was not likely to form because of better combustion conditions; any soot already present was burned off the window by the sun. No observation of the window or flame was possible during on-sun conditions. No changes are recommended.

6.5.1.5 Flame Monitoring. A unique problem that occurs with the solar reactor is the overexposure of the flickering IR flame detector when in on-sun operation. The flame safety

system then initiates a reactor trip and flame outage. The flickering IR detector works better with the VOC flame in on-sun conditions than with the LPG flame. Further development of the flame scanning techniques may involve the use of two or more flame detectors in parallel. The use of a flickering IR detector for off-sun operation and a UV or flame rod detector for on-sun operation may correct the flame detection problem.

6.5.1.6 Quench Design. In future field applications, the manual method gas sampling upstream of the scrubber that was conducted for this demonstration would not be necessary, so the external duct heating from the boom quench chamber to the scrubber could be eliminated. This would avoid additional PCDD/PCDF formation in the 80-foot to 100-foot section of ducting that is kept at temperatures between 150°C (300°F) and 260°C (500°F). In the field, a boom-mounted quench chamber would be used to completely quench the gases so downstream piping would be smaller and simpler and the scrubber quench chamber could be eliminated.

6.5.2 Technology Comparisons

The solar detoxification unit was demonstrated and evaluated as a stand-alone technology for treatment of VOCs and SVOCs. During an actual remediation project, the system would be used to destroy volatile contaminants removed from contaminated media. The system can be integrated with a soil remediation treatment train for on-site destruction of contaminants, or be used as a centralized destruction unit for off-site treatment of contaminants. Either application mode presents integration issues. Other contaminant treatment technologies either available or under development may be applied as well. This paragraph addresses the performance of solar detoxification and other technologies in addressing these integration issues.

6.5.2.1 Treatment Train Integration. The solar detoxification unit, as tested, can be integrated with a remedial system capable of supplying a condensed vapor stream. The solar detoxification unit would represent the end-member destructive element of a treatment train designed to transfer and concentrate volatile contaminants from the impacted media (soil and/or water). The extractive elements of the treatment train would remove contaminants *in situ* or operate *ex situ* on excavated soil. *In situ* technologies for removal of volatile contaminants from the subsurface include soil vapor extraction (SVE), air sparging, and *in situ* thermal treatments, such as steam-enhanced extraction and radio frequency heating. The predominant *ex situ* method for transferring contaminants from excavated soil is thermal desorption.

Selection of the solar detoxification unit as the end-member destructive element in a treatment train is dependent on site-specific issues involving performance, cost, social, and regulatory components, as well as the cost and performance of alternative destruction technologies.

A major consideration in selecting solar detoxification involves the mode of contaminant extraction and the mass of contaminants that need to be treated. Due to high mobilization and demobilization costs, on-site destruction would require a large and relatively constant supply of extracted contaminants for cost-effective treatment. Furthermore, *in situ* processes such as SVE will extract a large mass of contaminants during the early phase of a remedial project, but deliver lower fluxes of contaminants over time. SVE projects often initiate off-gas treatment with a destructive technology, such as catalytic oxidation, and switch to carbon adsorption and off-site

treatment during the latter phases of the project. The economics of on-site treatment are not justified during the latter stages of SVE. *Ex situ* processes, such as thermal desorption, can be engineered to provide a more constant contaminant loading over the course of the remedial project. This will ensure the destructive system is properly scaled to the contaminant flux over the entire life of the project.

Solar detoxification would be most applicable to sites providing relatively constant and large amounts of contaminants where mobilization and demobilization costs can be absorbed over the length of the project. For smaller volumes of impacted media, or sites with changing concentrations of extracted contaminants, other technologies may be preferred. These options include conventional processes such as catalytic oxidation, or innovative technologies such as biofilters and photocatalytic destruction. If necessary, these systems could be readily demobilized and replaced with carbon adsorption for off-site treatment during periods of lower contaminant flux.

6.5.2.2 Centralized Destruction Unit. To offset mobilization and demobilization costs of the solar detoxification unit for smaller remediation projects, the solar detoxification unit could be permanently installed as a centralized destruction facility. In this capacity, the unit would receive carbon-adsorbed waste transported from remediation projects located within a certain distance from the centralized unit. This would facilitate the development of more flexible remedial alternatives for site restoration. These alternatives could employ a combination of contaminant extraction and *in situ* destruction technologies. A possible scenario may utilize soil vapor extraction or air sparging followed by off-site destruction by solar detoxification, in combination with *in situ* bioremediation strategies (for example, bioventing, cometabolic bioremediation). Utilizing the solar detoxification unit as an off-site treatment technology would decouple it from site-specific contaminant extraction rates, which typically change over time.

6.5.2.3 Benefits and Limitations as Compared to Other Destruction Technologies. The selection of a remedial technology is dependent on a set of technical and economic conditions, which are site-specific and reliant on changing regulatory and social issues. Therefore, each technology has benefits and limitations, which dictate its selection in a changing remediation environment. The characteristics of the solar detoxification unit can be evaluated and compared to other existent and emerging technologies to ensure that solar offers a cost- and environmentally-responsible alternative.

The dominant promise of the solar detoxification technology is the reliance on a nonpolluting renewable resource as the energy source for the destructive process. This attribute is advantageous when compared to other thermal destruction technologies, which rely on a petroleum-based fuel to achieve destruction of contaminants. Depending on site-specific conditions, solar detoxification may not be technically superior or more cost-effective than conventional incineration or alternative thermal processes. However, the use of a renewable and nonpolluting energy source may be more important from a regulatory and public perspective.

There are several characteristics of the technology that may limit its selection for a specific remediation project. Technology application is limited to geographic locations with a high number of sun-days per year. In addition, the system cannot be continuously operated and is

dependent on specific insolation conditions. For on-site treatment, this may require storage of the condensed volatiles. Other competitive thermal technologies are not geographically limited and can run 24 hours a day. These systems may also be operated unattended as part of a vapor extraction treatment train. As previously discussed, high mobilization and demobilization costs may inhibit selection of solar detoxification for projects with a duration of less than one year. However, if applicable, a centralized treatment facility can be established to service several concurrent remedial projects.

There are several alternative conventional and emerging destructive technologies that can treat off-gases from SVE or are thermal destruction components of a treatment train. Table 6-6 provides a summary of some representative technologies (including solar detoxification) and identifies their strengths and weaknesses. It is important to note that this compilation does not include *in situ* technologies, which destroy or detoxify volatiles in the subsurface. This comparison is difficult due to the divergent site and contaminant conditions governing selection.

6.6 Economic Analysis

The capital cost estimate developed for the solar detoxification system was based on the actual costs incurred to manage the project, procure equipment, and install the solar detoxification prototype unit in Golden, Colorado. Equipment costs were provided by SAIC for the solar concentrator and SOE unit. Equipment costs were obtained from vendors for the reactor, quench system, venturi scrubber, auxiliary fuel and waste storage, personnel facilities, and instruments/controls/data acquisition. Engineering costs for the solar concentrator were estimated based on production of 100 identical units, with five of these being for soil detoxification applications. The engineering cost for the solar reactor and auxiliary supporting systems was based on one unit being built. The engineering cost shown therefore includes 100 percent of the actual cost incurred for the prototype reactor. All of the capital and operating costs shown in Table 6-7 are based on 1997 U.S. dollars.

The overall capital cost for a new system is estimated at \$767,783. Upon adding a 15 percent project contingency, the total plant investment is estimated at \$882,951. Annual operating costs were developed based on the detoxification of 13,300 gallons of organics stripped from 55,000 cubic yards of soil containing 0.1 weight (wt) percent hazardous-toxic organics and for 300 on-sun operation days per year. The total annual operating cost is estimated at approximately \$271,988. Labor, plus administration, and general overhead make up some 60 percent of the total operating cost.

Based on the capital and operating costs developed, a discounted cash flow (DCF) rate of return on investment (ROI) analysis was made based on the following assumptions:

- 15-year project/equipment life
- 15-year Modified Accelerated Cost Recovery System (MACRS)

Table 6-6. Comparative Assessment of Technologies for the Treatment of Extracted VOCs

Technology	Description	Benefits	Limitations
Incineration	High temperature destruction of organic contaminants	<ul style="list-style-type: none">• Established technology• Can achieve DREs• Multiple vendors	<ul style="list-style-type: none">• Reliant on external energy source• Negative public perception• High mobilization/de-mobilization costs• Possible dioxin/furan formation
Solar Detoxification	Lower temperature (as compared to incineration) destruction of organics using solar energy	<ul style="list-style-type: none">• Renewable energy source• Less polluting energy source	<ul style="list-style-type: none">• Geographically limited• Cannot be continuously operated• High mobilization/de-mobilization costs• Possible dioxin/furan formation
Catalytic Oxidation	Lower temperature (as compared to incineration) destruction of organics using thermal and catalytic processes	<ul style="list-style-type: none">• Easily transportable• Low mobilization/de-mobilization costs• Suitable for small remediation projects• Can operate unattended	<ul style="list-style-type: none">• Reliant on external energy source• May not achieve DREs
Biofilters	Volatile components in off-gas are biologically degraded by microorganisms	<ul style="list-style-type: none">• Non-thermal process• Low capital cost• Suitable for low contaminant flux	<ul style="list-style-type: none">• Effectiveness depends on biological processes that vary based on type and concentration of contaminant• Temperature may effect performance
High Energy Corona	High voltage electricity destroys volatiles at room temperature	<ul style="list-style-type: none">• Low temperature process	<ul style="list-style-type: none">• Not evaluated at full-scale
Photolytic Destruction	Volatile components are photolyzed and the by-products react with a solid reagent substrate	<ul style="list-style-type: none">• Non-thermal process• Operates at low pressure and temperature• Transportable	<ul style="list-style-type: none">• Produces a solid residual that must be disposed• Low concentration off-gas streams must be concentrated

Note:

DRE = destruction and removal efficiency

Table 6-7. Solar Detoxification System

Category	CAPITAL COST
	Cost*
Equipment:	
Reactor/Quench Vessel	\$105,294
Venturi Scrubber (assembled package unit)	\$78,353
Solar Concentrator	\$55,044
Fuel/Waste Storage/Utilities/Personnel Facilities	\$32,378
Instrumentation/Controls/Data Acquisition	\$39,129
Subtotal	\$310,198
Engineering	\$200,599
Purchasing	\$23,130
Construction	\$92,134
Project/Construction Management	\$57,600
Freight	\$15,510
Taxes & Permits/Remedial Action Plan	\$68,612
Total	\$767,783
Project Contingency @ 15%	\$115,167
Total Plant Investment (TPI)	\$882,950

* 1997 U.S. Dollars

ANNUAL OPERATING COST*

{ Annual Organic Destruction = 13,300 gallons or 53.15 tons }
 { Approx. 55,500 yd³ of soil treated per year @ average of 0.1 wt% organics }

	Annual Use	Cost/Unit	Cost/ Yr	\$/gal	\$/ton
Raw Material:					
Propane	120 MM Btu	\$4.20 /MM Btu	\$504	0.04	9
Sodium Hydroxide (50 wt% NaOH)	13,082 gal	\$1.20 /gallon**	\$15,698	1.18	295
Utilities:					
Electricity	2,378 kWhr	\$0.07 /kWhr	\$166	0.01	3
Water	170 Mgal	\$2.28 /Mgal	\$388	0.03	7
Disposal:					
Scrubber Effluent	142 Mgal	\$22.00 /Mgal	\$3,118	0.23	59
Labor:					
Operating	2,362 mnhrs	\$15 /mnhr	\$35,430	2.66	667
Maintenance @ 60% of 2.5% of TPI			\$13,244	1.00	249
Supervision	2,362 mnhrs	\$25 /mnhr	\$59,050	4.44	1,111
Testing/Analytical:					
Laboratory analyses, stack & soil testing			\$40,000	3.01	753
Supplies:					
Operating @ 20% of Operating Labor			\$7,086	0.53	133
Maintenance @ 40% of 2.5% of TPI			\$8,830	0.66	166
Administrative and General Overhead (60% of total labor):			\$64,635	4.86	1,216
Insurance and Taxes (2.7% of TPI):			\$23,840	1.79	449
Total Operating Costs			\$271,988	20.45	5,117

* Basis for annual capacity, 500 Langley's/day average annual solar energy (1 Langley = 1 gmcal/cm²) w/overall solar capture efficiency of 88% at 300 days per year of solar reactor operation (2,362 hours per year, 7.87 hrs/day at 200,000 Btu/hr average solar energy input to reactor.

** NaOH @ \$370/dry ton

- Working capital: Sum of raw materials at 14 days at full rate, plus materials and supplies; 0.9 percent of total plant investment, plus net receivables at 1/24 sales revenues
- Startup cost at 20 percent of total operating cost.

The lowest cost of remediation would be found in a condition in which the unit operated for its 15-year life at one location. In actual practice, there would be several site remediations using this equipment ranging each in project life from 6 months to 5 years or more. The shorter the project life, the more costly the solar detoxification system will become because of the mobilization/demobilization costs as a function of total organics destroyed over the life of the project.

The cost of solar detoxification, based on a 20 percent DCF-ROI over the 15-year equipment life for projects ranging from 6 months to 15 years is shown in Figure 6-10. This projection includes mobilization/demobilization costs. For a 6-month project, the cost of detoxification would be \$61.50 per gallon, about 1/3 greater than that for a 5-year project at \$46 per gallon. For a 15-year project life, the cost drops to its minimum of \$44.20 per gallon.

The cost of detoxification will be sensitive to availability of solar energy to support operations. The cost estimate is based on 300 days per year operation. If the system is located at a site with less solar availability, the annual treatment rate will be reduced. Materials, utilities, and disposal costs are incurred on demand and track the actual utilization of the facility. Labor costs will be incurred at nearly fixed rates because of the need to provide continuity for administrative and maintenance functions. Capital costs likewise will remain fixed. Therefore, the cost of solar detoxification will show an inverse dependence on capacity utilization or operating days per year. Sites with less solar availability will experience higher costs per gallon of waste treated.

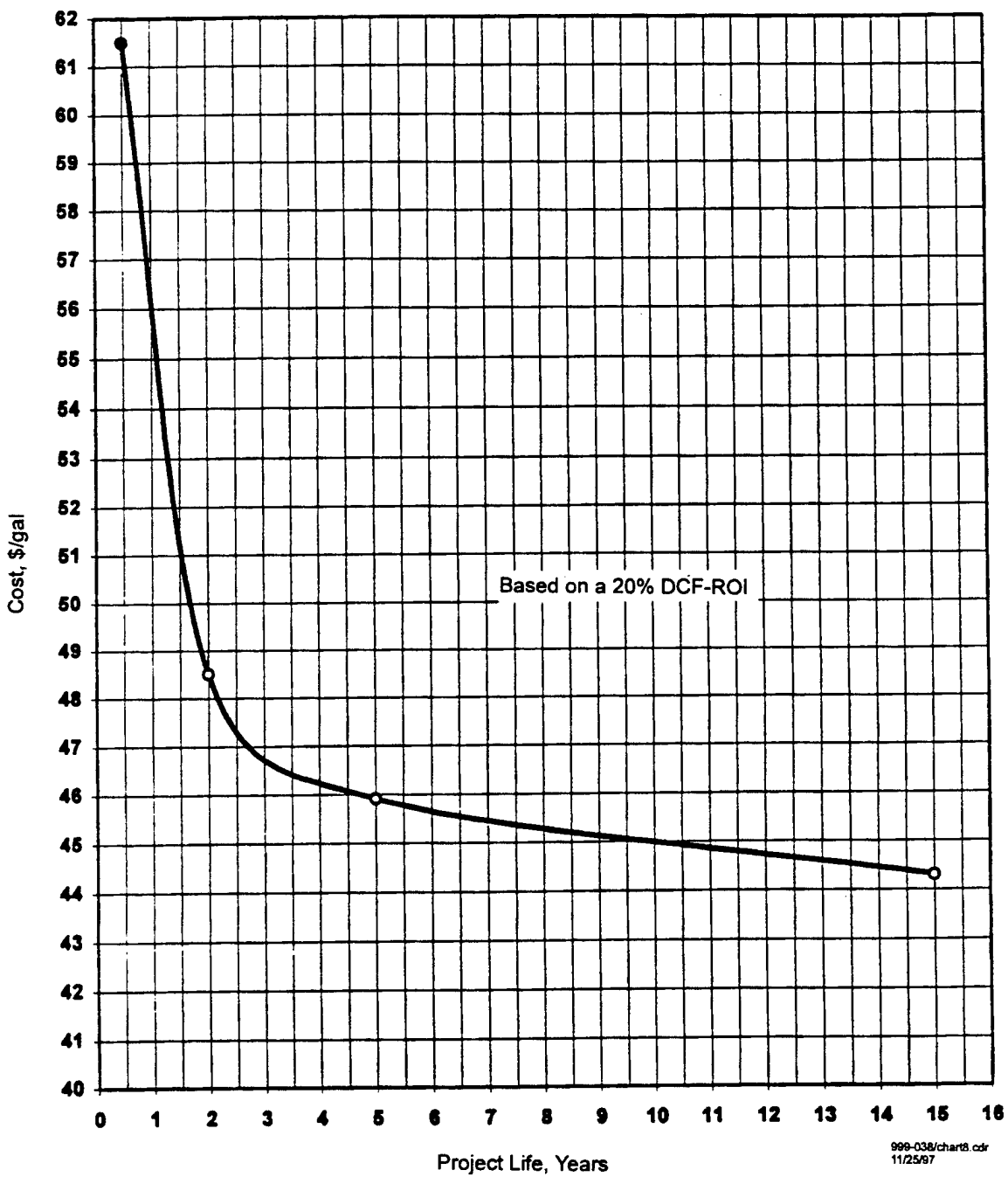


Figure 6-10. Solar Detoxification Cost Versus Project Life

7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The purpose of this demonstration test was to evaluate the use of solar energy to thermally detoxify organic compounds removed from contaminated media by *ex situ* (such as thermal desorption) or *in situ* (such as soil vapor extraction) treatment systems, or desorbed from pretreatment matrices (such as activated carbon). The demonstration results, discussed in Section 6, indicate that the test series successfully demonstrated a number of key aspects of the technology. For example, the tests demonstrated such key factors as efficient solar collection, concentration, and integration of solar energy input into a waste detoxification system. During testing, the solar dish collector tracking system operated well over the entire tracking path, and the quartz window and reactor chamber performed well under high intensity solar insolation. Other aspects of system design and performance will require improvement; however, before final conclusions are reached about the ultimate effectiveness of this type of system for destruction of organics removed from contaminated soils.

The solar detoxification system met the 99.99 percent DE criteria for seven of the eight POHCs, even under altered test conditions that resulted in increased residence times and decreased reactor temperatures. The goal of 99.99 percent or better DE for total POHCs was also met in eight of the nine test runs. However, the DE for one surrogate VOC, carbon tetrachloride, ranged from 99.95334 to 99.99653 percent under the test conditions. Within the test limitations, a statistically significant impact could not be directly attributed to the input of solar energy to the system: average DEs obtained during on-sun testing, using stoichiometries of 1.2 to 1.4, ranged from 99.99685 to 99.99951 percent, while average DEs for off-sun testing, using the same stoichiometries, ranged from 99.99962 to 99.99981 percent. Interpretation of these subtle differences was further complicated because calculated DEs greater than 99.99 percent may be attributable to high analytical detection limits or variability in analytical detection limits. Based on the current data, the DEs for the eight POHCs were not improved by solar input.

It was anticipated that solar detoxification would generate significantly lower levels of PICs than those measured in emissions from commercial incinerators. The system did not achieve this during the demonstration test. Test data could not be used to positively identify the cause(s) of the higher than anticipated PIC formation. It is possible these measurements were affected by specific design features of the test assembly [for example, higher than normal exhaust duct gas temperature and the length (80 to 100 feet) of the exhaust duct]. Additional design and testing would be required to confirm this. The emissions from the reactor were above standards for PCDD/PCDF (PICs), however actual emissions to the atmosphere are expected to be lower in an optimized operating system, since additional treatment steps would occur. In general, these tests indicate the system produced PICs at levels comparable to commercial incineration units, consistent with the test objective.

In general, the system met the test objectives for pollutant emissions. As expected, the reactor produced very low NO_x emissions, meeting the NSPS and medical waste standards during all nine tests; this was likely due to the low operating temperature range. Total emissions of THC

and HCl were also below regulatory standards during all tests, meeting the objectives for the demonstration. CO emissions varied from 12 to 673 ppmv during the tests, but met the regulatory goal of 50 ppmv during five of the nine tests. There was some indication that low stoichiometry and high solar insolation may reduce CO emissions; however, optimization studies are needed to ensure CO can be properly controlled during operations.

There are several characteristics of the technology that may limit its selection for a specific remediation project. Application of this technology is limited to geographic locations with a high number of sun-days per year. In addition, the system cannot be continuously operated and is dependent on specific insolation conditions. For on-site treatment, this may require storage of condensed volatiles. As noted in Section 6, high mobilization and demobilization costs may inhibit selection of solar detoxification for projects with a duration of less than 1 year. However, if applicable, a centralized treatment facility can be established to service several concurrent remedial projects.

7.2 Recommendations

Heat losses from the reactor proved to be larger than anticipated in the design, leading to reduced operating temperature and flame stability issues within the reactor. Through reduction of surrogate waste feed rate, limitations on excess air, and use of auxiliary fuel, stable operations were obtained for the test. During the on-sun demonstration tests, combustion was stabilized by the combination of the LPG pilot flame and solar insolation. Refinements to reactor design may lead to flame stability without the use of the auxiliary fuel pilot and increase throughput capacity. Recommendations for improvement to system design are provided below:

- *Eliminate the Cooling-Water Entrance Region.* This change is expected to decrease heat losses and improve flame stability so that the LPG pilot flame will not be needed during on-sun waste firing operations. This modification would also increase reactor gas temperatures and improve waste destruction but could lead to increased NO_x formation. Higher excess air levels, such as those initially selected in the design, could be used to moderate the flame temperature and control NO_x formation.
- *Eliminate the External Heating of the Duct from the Boom-Mounted Quench Chamber to the Scrubber.* This heated duct was required for the demonstration because flue gas samples were extracted upstream of the scrubber. However, in typical field applications this would not be necessary. The modification would involve utilizing the boom-mounted quench chamber to cool the gas and initially knock out acids. The colder gases could then be transported through smaller diameter acid-resistant fiberglass or polymer ducting, significantly reducing the cost and complexity of the ducting and potentially reducing downstream PCDD/PCDF formation.
- *Install Flame Detectors that can Work During Off-Sun and On-Sun Conditions.* The flickering IR sensor was overloaded with solar IR during LPG firing, while performing slightly better with waste firing. Therefore, multiple sensors may be

necessary to detect the flame during off-sun and on-sun conditions. During on-sun conditions, a flame rod or UV sensor could be used to detect a flame, while the flickering IR sensor would work well in off-sun and certain on-sun conditions.

7.3 Summary Assessment

While the test program provided insights concerning the viability of the solar detoxification system, there are several additional items that should be investigated.

- While the surrogate waste was well selected for consideration of performance, any field application would encounter significant variability in feed that could affect the performance. In particular, the Btu value of the proposed feed could be an important determinant of performance for this low temperature system. The potential for feeds with inorganics and metals might have to be tested also.
- The test measurement arrangements may have contributed to the development of PCDDs/PCDFs. Because this is such an important aspect of incineration technology, additional investigation of the formation of PCDDs/PCDFs within the process itself would need to be investigated.
- The data were collected under controlled conditions; however, measurements were not always taken when clouds altered the reactor temperature conditions. In a field application with an improved reactor design that provides greater DEs for on-sun than off-sun operations, the variability in solar input would be a critical factor for reactor control. Additional testing would be required to determine the impact of variations in solar flux on all measured parameters and the resultant control elements that would be required.
- Detailed measurements of the post-exhaust gas subsystem emissions need to be conducted to determine the total potential pollutants that would be emitted from this type of facility.
- Some design changes have been suggested as a result of this test program. It is possible that these changes could eliminate the need for a constant pilot flame from any external fuel. If these changes were to be considered, additional testing would be required to evaluate improvements in system performance. If the pilot flame cannot be eliminated from normal operation of the solar reactor, the solar detoxification system provides no significant technical performance improvement over incineration at increased cost.

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